

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Date: May 15, 2008

Applicants: Bednorz et al.

Docket: YO987-074BZ

Serial No.: 08/479,810

Group Art Unit: 1751

Filed: June 7, 1995

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Commissioner for Patents

United States Patent and Trademark Office

P.O. Box 1450

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**APPEAL BRIEF
PART IX**

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SECTION 1

VOLUME 4

Part 4

BRIEF ATTACHMENTS P TO Z

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BRIEF ATTACHMENT P

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FIRST SUPPLEMENTAL AMENDMENT

Sir:

In response to the Office Action dated July 28, 2004, please consider the
following:

ATTACHMENT P

LANDOLT-BÖRNSTEIN

LA

Numerical Data and Functional Relationships
in Science and Technology

New Series

Editor in Chief: K.-H. Hellwege

Group III: Crystal and Solid State Physics

Volume 3

Ferro- and Antiferroelectric Substances

by Toshio Mitsui and

R. Abe · Y. Furuhata · K. Gesi · T. Ikeda · K. Kawabe

Y. Makita · M. Marutake · E. Nakamura · S. Nomura

E. Sawaguchi · Y. Shiozaki · I. Tatsuzaki · K. Toyoda

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Sprir

II Data

Oxides

1 Perovskite-type oxides

1A Simple perovskite-type oxides

Nr. 1A-1 NaNbO_3 , Sodium niobate

a	It was reported by MARTIAS et al. in 1951 that NaNbO_3 was ferroelectric. Cross et al., however, proved in 1955 that at room temperature it is not ferroelectric but antiferroelectric.					51M2 55C2
b	phase	V	IV	III*	II	I
	state	F	A			P
	crystal system	monoclinic	orthorhombic	pseudo-tetragonal	tetragonal	cubic
	space group		Pbma^a - D_{2h}^{11}			$\text{Pm}3\text{m-O}_h^1$
	Θ^{**}	-200	354	562	640	a)61W2 58R3
	$P_r \parallel [001]$ in phase V. Phase IV: $a = 5.568 \text{ \AA} (\cong \sqrt{2}a_0)$, $b = 5.505 \text{ \AA} (\cong \sqrt{2}a_0)$, $c = 15.518 \text{ \AA} (\cong 4a_0)$, where a_0 is the lattice constant of the cubic cell of phase I. In phase IV (orthorhombic system) the longest edge of a unit cell is taken as the c axis (see Fig. 1). This system of the axes is adopted here. In Well and Megaw's analysis b and c axes were interchanged. The orthorhombic structure is also represented by a pseudomonoclinic unit cell (see Fig. 1), where $b' = c$, $a' = c' (\cong a_0)$, $\beta' \cong \pi/2$.					51V3 61W2
2a	Cooling method from a molten mixture of Na_2CO_3 , Nb_2O_5 , and NaF .					51W1
3	Crystal structure: In phase IV, $Z = 8$. Tab. 1; Fig. 1, 2.					
4	Lattice distortions (thermal expansion): For phase I, II, III, IV: Tab. 2,3; Fig. 3. For phase V, at -160°C : $a = 5.564 \text{ \AA} (\cong \sqrt{2}a_0)$, $b = 5.548 \text{ \AA} (\cong \sqrt{2}a_0)$, $c = 7.812 \text{ \AA} (\cong 2a_0)$, $\beta = 91^\circ 09'$. Fig. 4.					57J1
5a	Dielectric constants: Fig. 5. Curie-Weiss law: $\kappa = C/(T - \Theta_p)$, $T > \Theta_{\text{III-IV}}$, where $C = 2 \cdots 4 \cdot 10^5 \text{ } ^\circ\text{K}$ and $\Theta_p = 60 \cdots 80^\circ\text{C}$.					54S3 55C2
c	Spontaneous polarization: $P_s \cong 12 \cdot 10^{-3} \text{ C m}^{-2}$ ($\parallel c$, in phase V). Coercive and critical field for normal and double hysteresis curve: Fig. 6.					
9a	Birefringence: Fig. 7, 8.					
14a	Domain structure: See					55C2, 64p1, 62M9, 62W3
b	Dynamic properties: Fig. 9, 10.					

Tab. 1. NaNbO_3 . Fractional coordinates x, y, z of atoms in unit cell at RT. [61W2]

	x	y	z
Na(1)	$\frac{1}{2}$	0.250	0
Na(2)	0.769	0.251	$\frac{1}{2}$
Nb	0.261	0.257	0.125
O(1)	$\frac{1}{2}$	0.208	0
O(2)	0.271	0.290	$\frac{1}{2}$
O(3)	0.010	0.532	0.121
O(4)	0.446	0.972	0.126

* According to Ismailzade phase III consists of 4 phases (see Fig. 3). [63I4]

Transitions exhibit large temperature hysteresis, and the transition temperatures measured with decreasing temperature are given here.

Tab. 2. NaNbO_3 . Lattice parameters at various temperatures. [56F1] and [54S3]

$T [^\circ\text{C}]$	Crystal symmetry	Lattice parameters	
		[56F1]	[54S3]
20	Monoclinic	$a' = c' = 3.914 \text{ \AA}$ $b' = 4 \cdot 3.881 \text{ \AA}$ $\beta' = 90^\circ 39'$	$a' = c' = 3.915 \text{ \AA}$ $b' = 4 \cdot 3.881 \text{ \AA}$ $\beta' = 90^\circ 40'$
390	Pseudotetragonal	$a = 2 \cdot 3.920 \text{ \AA}$ $c = 4 \cdot 3.926 \text{ \AA}$ $c/a = 2.0032$	$a = 2 \cdot 3.919 \text{ \AA}$ $c = 4 \cdot 3.927 \text{ \AA}$ $c/a = 2.0040$
420	Pseudotetragonal	$a = 2 \cdot 3.924 \text{ \AA}$ $c = 4 \cdot 3.924 \text{ \AA}$ $c/a \approx 2.0000$	$a = 2 \cdot 3.921 \text{ \AA}$ $c = 4 \cdot 3.927 \text{ \AA}$ $c/a = 2.0028$
560	Tetragonal (changing to simple perovskite-type cell)	$a = 2 \cdot 3.933 \text{ \AA}$ $c = 4 \cdot 3.940 \text{ \AA}$ $c/a = 2.0038$	— — —
640	Cubic	$a = 3.942 \text{ \AA}$	—

Tab. 3. NaNbO_3 . Lattice parameters of the subcell at various temperatures. [63I4]. See Fig. 3

$T [^\circ\text{C}]$	Subcell parameters				
	pseudomonoclinic I ($a' = c' > b'$, $\beta' > 90^\circ$)				
	$a' [\text{\AA}]$	$b' [\text{\AA}]$	$\beta' - 90^\circ$	a'/b'	$V [\text{\AA}^3]$
18 ... 20	3.914 ₇	3.885	40'	1.0075 ₅	59.5 ₃
100	3.917 ₆	3.893 ₆	37	1.0060	59.7 ₄
150	3.919 ₆	3.898 ₇	33	1.0055	59.9
200	3.922 ₄	3.902 ₄	29	1.0050	60.0 ₅
250	3.924 ₃	3.907 ₅	26	1.0040	60.1 ₇
300	3.925 ₅	3.914	22	1.0030	60.3 ₃
340	3.926 ₅	3.917 ₆	18	1.0025	60.4
350	3.926 ₅	3.919	17	1.0020 ₂	60.4 ₂
pseudomonoclinic II					
360	3.927 ₂	3.920	6	1.0020	60.45
380	3.927 ₈	3.921 ₃	5	1.0015 ₆	60.50
400	3.928 ₂	3.922 ₃	4	1.0015	60.5 ₂
pseudomonoclinic III					
420	3.929 ₄	3.923	3	1.0015	60.5 ₅
440	3.930	3.924	3	1.0015	60.60
460	3.932	3.926 ₃	3	1.0015	60.70
pseudomonoclinic IV					
480	3.933 ₅	3.927 ₅	3	1.0015 ₂	60.7 ₇
500	3.934 ₅	3.928 ₈	2	1.0015	60.8 ₂
510	3.935	3.929 ₅	2	1.0015	60.85
tetragonal I					
$T [^\circ\text{C}]$	$c [\text{\AA}]$	$a = b [\text{\AA}]$	c/a	$V [\text{\AA}^3]$	
520	3.936 ₇	3.929 ₅	1.0015 ₅	60.80	
540	3.938	3.930 ₂	1.0020	60.85	
560	3.939 ₈	3.931 ₆	1.0020 ₈	60.90	
tetragonal II					
580	3.941 ₄	3.934 ₂	1.0020	61.00	
600	3.943 ₄	3.937 ₆	1.0015	61.15	
620	3.945 ₆	3.942	1.0010	61.30	
630	3.945	≈ 3.945	≈ 1.0000	61.40	
cubic					
$T [^\circ\text{C}]$	$a_0 [\text{\AA}]$	$V [\text{\AA}^3]$	$T [^\circ\text{C}]$	$a_0 [\text{\AA}]$	$V [\text{\AA}^3]$
640	3.947 ₂	61.50	700	3.949 ₇	61.6 ₃
650	3.947 ₆	61.5 ₂	720	3.950 ₆	61.6 ₇
680	3.949	61.5 ₇			

Furuhata/Marutake

Nr. 1A-2 KNbO₃, Potassium niobate

1a	Ferroelectricity in KNbO ₃ was first discovered by MATTHIAS in 1949.				49M4
b	phase	IV	III	II	I
	state	F	F	F	P
	crystal system	rhombohedral	orthorhombic	tetragonal	cubic
	space group		Bmm2 ^a)-C _{2v} ¹⁴		Pm3m-O _h ¹
	θ	-10	225	435	°C
	$P_s \parallel [001]$ in phase II (along [001] of phase I), $P_s \parallel [001]$ in phase III (along [110] of phase I), $P_s \parallel [111]$ in phase IV (along [111] of phase I). $T_{\text{melt}} = 1050^\circ\text{C}$ $\rho = 4.590 \cdot 10^3 \text{ kg m}^{-3}$ $a = 5.697 \text{ \AA}$, $b = 3.971 \text{ \AA}$, $c = 5.720 \text{ \AA}$ at RT. Transparent. Light yellow.				*)63K2 55R3, 58M3 52L1 67K4
2	Flux method (K ₂ CO ₃ flux). Phase diagram of K ₂ CO ₃ -Nb ₂ O ₅ system; see Pulling method from the K ₂ CO ₃ -Nb ₂ O ₅ mixture Crystal form: square plate				51W1 55R3 58M3
3	Crystal structure: $Z = 1$ in phase I, II, IV. $Z = 2$ in phase III. Tab. 4, 5; Fig. 11.				
4	Temperature dependence of lattice parameters: Tab. 6; Fig. 12.				
5	Dielectric constant: Fig. 13, 14. $\kappa = C/(T - \Theta_p)$, $T > \Theta_{\text{II-I}}$, where $C = 2.42 \cdot 10^5 \text{ }^\circ\text{K}$, $\Theta_p = 360^\circ\text{C}$. Nonlinear dielectric properties: $\xi = -1.62 \cdot 10^9 \text{ J C}^{-4} \text{ m}^5$, $\zeta = 1.79 \cdot 10^{10} \text{ J C}^{-6} \text{ m}^9$. Spontaneous polarization and coercive field: Fig. 15. $P_s = 26 \cdot 10^{-2} \text{ C m}^{-2}$ at $T = \Theta_p$.				56T3 56T3 56T3 56T3
6	Transition heat, transition entropy: Tab. 7.				56T3
7	Piezoelectricity: Fig. 16.				
12	NQR: Tab. 8; Fig. 17 ... 20.				

Tab. 4. KNbO₃. Atomic positions in fractional coordinates at RT in phase III. [67K4]

Nb	0, 0, 0
K	$0, \frac{1}{2}, \frac{1}{2} + z_K$
O(1)	$0, \frac{1}{2}, z_1$
O(2)	$\frac{1}{2} + x_2, 0, \frac{1}{2} + z_2$
z_K	+0.017
z_1	+0.021
z_2	+0.035
x_2	+0.004

Tab. 5. KNbO₃. Interatomic distances and bond angles at RT. [67K4]

	*	distance Å	**	*	angle °
Nb-O(1)	(2)	1.991 ± 0.001	O(2)(s)-Nb-O(2)(s)	(1)	97.4 ± 1.2
Nb-O(2)	(2)	1.863 ± 0.007	O(2)(l)-Nb-O(2)(l)	(1)	83.4 ± 1.0
Nb-O(2)	(2)	2.180 ± 0.009	O(2)(s)-Nb-O(2)(l)	(2)	89.7 ± 0.5
K-O(1)	(1)	2.837 ± 0.014	O(1)-Nb-O(2)(s)	(4)	92.3 ± 0.6
K-O(1)	(2)	2.848 ± 0.001	O(1)-Nb-O(2)(l)	(4)	87.5 ± 0.6
K-O(1)	(1)	2.883 ± 0.014	Nb-O(1)-Nb	(1)	172.8 ± 0.7
K-O(2)	(4)	2.792 ± 0.008	Nb-O(2)-Nb	(2)	168.6 ± 0.6
K-O(2)	(4)	2.873 ± 0.010			
O(1)-O(2)	(4)	2.780 ± 0.012			
O(1)-O(2)	(4)	2.884 ± 0.012			
O(2)-O(2)	(1)	2.802 ± 0.024			
O(2)-O(2)	(1)	2.894 ± 0.024			
O(2)-O(2)	(2)	2.860 ± 0.001			

* Numbers in this column indicate numbers of equal bonds or angles per formula unit.

* For the O-Nb-O angles, the letter s or l indicates whether the Nb-O(2) bond involved is short or long.

Tab. 6. KNbO_3 . Lattice constants and volume of unit cell at various temperatures. [54S3]. a' , c' : lattice parameters of pseudotetragonal cell

T °C	$a' = c'$ Å	b Å	b/a	β	V Å ³
25	4.0375	3.9711	1.0167	90° 15'	64.73
125	4.0374	3.9797	1.0145	90° 15'	64.87
185	4.0363	3.9830	1.0134	90° 13'	64.89
205	4.0369	3.9839	1.0133	90° 14'	64.93
	$a = b$	c	c/a		
220	3.9972	4.0636	1.0166		64.92
230	3.9978	4.0640	1.0166		64.95
270	3.9992	4.0647	1.0164		65.01
320	4.0023	4.0639	1.0154		65.10
375	4.0048	4.0620	1.0143		65.15
410	4.0080	4.0567	1.0122		65.18
425	4.0214				65.03
450	4.0225				65.09
510	4.0252				65.22

Tab. 7. KNbO_3 . Transition heat and transition entropy per mole. [54S7]

Transition	ΔQ_m cal mol ⁻¹	ΔS_m cal °K ⁻¹ mol ⁻¹
IV → III	32	0.12
III → II	85	0.17
II → I	190	0.28
	134	—

Tab. 8. KNbO_3 . NQR spectrum. [54C1]. The measured frequency ratios intersect the calculated ratios in a straight line at constant $\eta = 0.806 \pm 0.002$. η = asymmetry parameter

Crystal structure	f MHz	Measured ratio	Calculated ratio ($\eta = 0.806$)	Identification	e^2qQ/h MHz
orthorhombic (20 °C)	3.648			(9/2, 7/2)	23.120 ± 0.05
	3.030	1.204	1.204	(3/2, 1/2)	
	2.527	1.198	1.196	(7/2, 5/2)	
	2.085	1.214	1.213	(5/2, 3/2)	
rhombohedral (-196 °C)	2.674		($\eta = 0.0$)	(9/2, 7/2)	16.0 ± 0.1
	2.004	1.335	1.333	(7/2, 5/2)	
	1.335	1.503	1.500	(5/2, 3/2)	

Nr. 1A-3 NaTaO_3 , Sodium tantalate

1a	It was reported by MATTHIAS in 1949 that NaTaO_3 is ferroelectric below 480 °C. No anomalies of the dielectric constants, however, were observed by SMOLENSKII et al.					49M1 57S3
b	phase	IV	III	II	I	
	state	(F)				
	crystal system	orthorhombic	orthorhombic	tetragonal	cubic	57K1
	space group	$\text{Pc}2_1\text{n-C}_{2v}^2$				57K1
	θ	480	550	630	°C	6214 51V2
3	$a = 5.4941 \text{ Å}$, $b = 7.7508 \text{ Å}$, $c = 5.5130 \text{ Å}$ at RT. The cubic cell in phase I becomes pseudomonoclinic in phase IV. Relation between the orthorhombic unit cell and the pseudomonoclinic cell: Fig. 21.					
4	Crystal structure: $Z = 4$. Atomic positions: Tab. 9; Fig. 22. Temperature dependence of lattice parameters: Tab. 10; Fig. 23.					

Tab. 9. NaTaO₃. Fractional coordinates of atoms in the unit cell. [57K1]

Na	x :	$0 - 0.01$	$0 + 0.01$	$\frac{1}{2} - 0.01$	$\frac{1}{2} + 0.01$
	y :	$\frac{1}{4} + 0.03$	$\frac{1}{4} + 0.03$	$\frac{1}{4} + 0.03$	$\frac{3}{4} + 0.03$
	z :	$0 + 0.02$	$0 - 0.02$	$\frac{1}{2} - 0.02$	$\frac{1}{2} + 0.02$
Ta*	x :	$\frac{1}{2}$	$\frac{1}{2}$	0	0
	y :	0	$\frac{1}{2}$	$\frac{1}{2}$	0
	z :	0	0	$\frac{1}{2}$	$\frac{1}{2}$
O(1)	x :	$0 - 0.02$	$0 + 0.02$	$\frac{1}{2} + 0.02$	$\frac{1}{2} - 0.02$
	y :	$\frac{1}{4} + 0.01$	$\frac{1}{4} + 0.01$	$\frac{3}{4} + 0.01$	$\frac{1}{4} + 0.01$
	z :	$\frac{1}{2} + 0.02$	$\frac{1}{2} - 0.02$	$0 + 0.02$	$0 - 0.02$
O(2)	x :	$\frac{1}{4} + 0.04$	$\frac{1}{4} - 0.04$	$\frac{3}{4} - 0.04$	$\frac{3}{4} + 0.04$
	y :	$0 - 0.03$	$0 - 0.03$	$\frac{1}{2} - 0.03$	$\frac{1}{2} - 0.03$
	z :	$\frac{1}{4} + 0.04$	$\frac{3}{4} + 0.04$	$\frac{3}{4} - 0.04$	$\frac{1}{4} - 0.04$
O(3)	x :	$\frac{1}{4} + 0.04$	$\frac{1}{4} - 0.04$	$\frac{3}{4} - 0.04$	$\frac{3}{4} + 0.04$
	y :	$\frac{1}{2} + 0.06$	$\frac{1}{2} + 0.06$	$0 + 0.06$	$0 + 0.06$
	z :	$\frac{1}{4} + 0.04$	$\frac{3}{4} + 0.04$	$\frac{3}{4} - 0.04$	$\frac{1}{4} - 0.04$

Tab. 10. NaTaO₃. Temperature dependence of the pseudo-cell parameters. [62I4].
For the notations, see Fig. 21

T [°C]	23	100	200	300	400	450	480	500	550	580	600
$a' = c'$ [Å]	3.889 _s	3.893 _s	3.899 _s	3.907	3.912 _s	3.916	3.918	3.920	3.923	3.925 _s	3.927
b' [Å]	3.885 _s	3.890 _s	3.896 _s	3.903 _s	3.910 _s	3.913 _s	3.915 _s	3.918	3.923	≈3.925 _s	≈3.927
$\beta - 90^\circ$	22'00"	16'00"	9'00"	6'00"	4'00"	3'30"	2'00"	≈2'00"	1'30"	0'00"	0'00"
a'/b'	1.0010	1.0009	1.0009	1.0008	1.0006	1.0006	1.0005	1.0005	1.000	1.000	1.000
V [Å ³]	58.8 ₀	59.0 ₀	59.2 _s	59.5 _s	59.8 _s	60.0 ₀	60.1 ₀	60.2 ₀	60.3 _s	60.4 _s	60.5 _s

T [°C]	630	660	680
$b = a = c$ [Å]	3.929	3.931	3.932 _s
V [Å ³]	60.6 _s	60.7 _s	60.8 ₀

Nr. 1A-4 KTaO₃, Potassium tantalate

1a	Ferroelectric activity was first reported by MATTHIAS in 1949; ^{a)} however, recent studies by WEMPLE have proved that the ferroelectric transition does not occur, at least above 1.6 °K. ^{b)}	^{a)} 49M1, 49M4 ^{b)} 64W2, 65W2
b	KTaO ₃ is cubic and its space group is Pm3m-O _h . $T_{\text{melt}} = (1357 \pm 3)^\circ\text{C}$. $\rho = 6.97 \cdot 10^3 \text{ kg m}^{-3}$. $a = 3.9885 \text{ Å}$ at RT. Transparent, colorless or pale blue (blue in oxygen-deficient crystals). Cleavage: along (100) planes. Hardness: nearly the same as quartz.	64W2, 65W2, 51V2 55R2, 56R2 58R1 51V2 64W2
2a	Flux method: KF flux, ^{a)} dark small crystals; K ₂ CO ₃ flux, ^{b)} large (≈10 mm) transparent crystals. Czochralski-Kyropoulos method: large (≈10 mm) good quality crystals. Floating technique: planar single crystals. Phase diagram of system K ₂ CO ₃ -Ta ₂ O ₅ : Fig. 24. Hydrothermal phase diagram K ₂ O-Ta ₂ O ₅ -H ₂ O at 400 °C:	^{a)} 62T5, 64W2 ^{b)} 66U1 64W2, 65W2, 67B7 66W8 67M2
3	$Z = 1$ Crystal structure: cubic perovskite type, (Pm3m-O _h). K at 1a position; Ta at 1b position; 3O at 3c position.	51V1, 51V2

* All positions ±0.002.

Figuren S. 221 ff.

II 1 Oxide des Perowskit-Typs

4	Nr. 1A-4 KTaO_3 , continued $a = 3.9885 \text{ \AA}$ at RT; $a = 4.0026 \text{ \AA}$ at 450°C .	51V2, 59B1
5a	Dielectric constant at low frequencies: earlier studies showed a peak in the κ vs. T curve; ^{a)} recent measurements have shown that no peak exists down to 1.6°K . ^{b)} Fig. 25. $\kappa = 243$ at RT. $\kappa = \kappa_0 + C/(T - \Theta_p)$, $T > 30^\circ\text{K}$, where $\kappa_0 = 48$, $C = 5.7 \cdot 10^4^\circ\text{K}$, $\Theta_p = 4^\circ\text{K}$. Loss tangent: $\tan \delta \approx 0.001$ at 200 kHz at RT. Dielectric constant in the GHz range: Fig. 26. Q values in the GHz range: $Q = 10^3 \dots 10^4$. Dielectric loss in the far infrared frequency range: See 1A-4-9 below (Figs. 34, 35). Hydrostatic pressure dependence of the reciprocal dielectric constant: Fig. 27.	^{a)} 50H3 ^{b)} 65W2, 64W2 65W2 64W2 64R3 64W2
b	Effects of dc bias on κ at 4.2°K and at RT: Figs. 28, 29. Coefficients in free energy expansion: $\xi = 9 \cdot 10^9 \text{ V m}^5 \text{ C}^{-3}$ at 4.2°K , $\xi = (4 \pm 1) \cdot 10^9 \text{ V m}^5 \text{ C}^{-3}$ at 295°K .	65K1 65W2 64W2
c	D vs. E curves show no hysteresis character down to 1.6°K . P vs. E at 4.2°K : see	
9a	Refractive index in visible region: Fig. 30. Reflectivity in far infrared region and the dispersion: Figs. 31, 32. Reflectivity data were used to obtain transverse optical modes of the lattice vibration by means of Kramers-Kronig relation (cf. Tab. 42). Transverse optical modes as a function of temperature: Tab. 11; Fig. 33. The square of the wave number $\tilde{\nu}_{11}$ for the "ferroelectric mode" is approximately linear to T : $\tilde{\nu}_{11}^2 \propto (T - \Theta_p)$ (Additional data are given on the ferroelectric soft mode, see 1A-4-13b). Effect of lattice vibration on the fluorescent spectrum of Eu^{3+} in KTaO_3 : see Imaginary part of the dielectric constant and the conductivity in the far infrared region: Figs. 34, 35. Absorption coefficient α depends on the degree of oxygen reduction in KTaO_3 . Absorption coefficient near the interband absorption edge (about 3.6 eV) for insulating and semiconducting KTaO_3 : Fig. 36 (for additional data, see Fig. 2 of reference). Absorption vs. wavelength of light: Fig. 37. Absorption vs. carrier concentration in semiconducting KTaO_3 : Fig. 38. Optical absorption in impurity doped single crystals: for impurities Fe, Mn, Co and Cr, see	63M4, 67P4 67P4, 67F2 65S9 65W2 67B1 64W2 64G3, 63G3 67F4
b	Quadratic electrooptic constants (6328 \AA , $2 \dots 77^\circ\text{K}$): $M_{11} - M_{12} = (0.16 \pm 0.01) \text{ m}^4 \text{ C}^{-2}$; $M_{44} = (0.12 \pm 0.01) \text{ m}^4 \text{ C}^{-2}$. Electroreflectance and electroabsorption were studied using semiconducting KTaO_3 . Effect of interface dc field on the reflectance of the (100) surface: Fig. 39. Electroreflectance spectra of (100) and (111) surfaces: Figs. 40, 41. Effect of polarization of light on the electroreflectance: Fig. 42. Electroreflectance as a function of the surface polarization: Fig. 43. Electroreflectance singularities and the corresponding energies: Tab. 12. Electroabsorption near the absorption edge: Fig. 44. Fundamental absorption edge ($\approx 3.6 \text{ eV}$) shifts to higher energies with dc bias: Fig. 45.	67B1, 66B2 67F2
d	Faraday rotation near the band edge: Fig. 46; Tab. 44.	
f	Electric-field-induced Raman effect: Fig. 47. (For the ferroelectric soft mode obtained from the Raman scattering, see Fig. 33). Fluorescence spectrum of Eu^{3+} in KTaO_3 : see	65S9
10	Resistivity of insulating single crystal: $\rho > 10^9 \Omega \text{ m}$ at RT. Most data on the transport properties have been obtained using oxygen-deficient semiconducting KTaO_3 . Resistivity of oxygen-deficient single crystals as a function of temperature: Fig. 48. Hall mobility: $\mu_H = 3 \cdot 10^{-3} \text{ m}^2 \text{ V}^{-1} \text{ sec}^{-1}$ at RT (see also Tab. 13). $\mu_H \approx 8 \cdot 10^4 \text{ T}^{-3} \text{ m}^2 \text{ V}^{-1} \text{ sec}^{-1}$, $T > 100^\circ\text{K}$; Fig. 49. Hall coefficient and Hall mobility at 4.2°K and RT for several semiconducting KTaO_3 : Tab. 13. Hall mobility vs. carrier concentration: Fig. 50. Scattering cross section vs. carrier concentration: see Ca concentration in doped KTaO_3 vs. net ionized donor concentration: see Electrical conductivity vs. hydrostatic pressure: Fig. 51. Conductivity in the far infrared region: see Fig. 35. Seebeck coefficient: $Q = 550 \mu\text{V } ^\circ\text{K}^{-1}$ at RT. (Oxygen-deficient KTaO_3 with $N = 3.5 \cdot 10^{23} \text{ m}^{-3}$). Effective mass estimated from the Seebeck coefficient: $m^* = (0.8 \pm 0.28) m_0$. Photoconductivity vs. $h\nu$ shows a peak at $h\nu = 3.58 \text{ eV}$.	65W2 65W2 65W2 66S17 66W5 65W2 65W2 65W2

Sawaguchi

12a	Nr. 1A-4 KTaO_3 , continued
b	Dielectric constant at low frequencies: earlier studies showed a peak in the κ vs. T curve; ^{a)} recent measurements have shown that no peak exists down to 1.6°K . ^{b)} Fig. 25.
13b	Effects of dc bias on κ at 4.2°K and at RT: Figs. 28, 29.
17	Refractive index in visible region: Fig. 30.
Tab. mode The soft 1	
T [°K]	
12a	
12b	
23a	
29a	
46a	

12a	NMR of ^{181}Ta in KTaO_3 : spin-lattice relaxation time, $T_1 \approx 10^{-3}$ sec at RT; spin-spin relaxation time, $T_2 = \approx 10^{-5}$ sec at RT; nuclear magnetic moment of ^{181}Ta ($I = 7/2$): $p_n = (2.340 \pm 0.001) \mu_n$ (uncorrected); ($p_n = (2.35 \pm 0.01) \mu_n$, after estimated corrections). Nuclear magnetic acoustic resonance: the absorption data were given for $\Delta m = \pm 2$ transition of ^{181}Ta as a function of the angle between magnetic field and sound axis [100].	60B2 67M4 66U1 64W2 67H3 67H3 63W5, 64W2 67H3, 65H2 64W2															
b	ESR of Eu^{2+} and Gd^{3+} in KTaO_3 : Tab. 14. ESR of Fe^{3+} : $g = 1.99 \pm 0.01$; $ a = (345 \pm 10) \cdot 10^{-2} \text{ m}^{-1}$ at 4.2 °K; $a = (288 \pm 5) \cdot 10^{-2} \text{ m}^{-1}$ at RT (Fe^{3+} is on the Ta^{5+} site). $a = (30 \pm 1) \cdot 10^{-2} \text{ m}^{-1}$ at RT (Fe^{3+} is on the K^{1+} site). ESR Stark effect for Fe^{3+} : E_{bias} along [100] induces axial splitting term D ($D = 12 \cdot 10^{-2} \text{ m}^{-1}$ at $E_{\text{bias}} = 1.0 \text{ MV m}^{-1}$ at 4.2 °K; $D \propto E_{\text{bias}}^2$). ESR of Ni^{3+} located on Ta^{5+} site (low spin state) and on K^{1+} site: see ESR in Mn-doped, Co-doped and Cr-doped KTaO_3 : see																
13b	Phonon dispersion relation for the transverse optical branch: Fig. 52; Tab. 15. Temperature dependence of the ferroelectric soft mode: Fig. 53. The square of the phonon energy of the ferroelectric soft mode can be approximated by $(\hbar\nu)^2 = 10^4 A/\kappa$, $40^\circ\text{K} < T < 295^\circ\text{K}$; where $A = 2.825 (\text{meV})^2$, $\kappa(T)$ is the dielectric constant. For the ferroelectric soft mode, see also 1A-4-9a. Phonon energies of the acoustic modes: Fig. 54.	67S11 67S11															
17	Etchant: single crystal is slowly etched by dilute HF. Band structure and the related properties: see references; also 1A-4-9a, 9b, 9d, 10, and Tab. 12. Band gap energies determined by various methods:	64W2 67F4, 67B1															
<table border="1"> <thead> <tr> <th>Method</th><th>296 °K</th><th>77 °K</th></tr> </thead> <tbody> <tr> <td>Faraday rotation</td><td>3.77 eV 3.62 eV</td><td>3.79 eV 3.65 eV</td></tr> <tr> <td>Electroreflectance singularities</td><td>3.57 eV 3.80 eV</td><td></td></tr> <tr> <td>Absorption data</td><td>3.75 eV</td><td></td></tr> <tr> <td>Energy at which $\alpha \approx 10^6 \text{ m}^{-1}$</td><td>3.79 eV</td><td></td></tr> </tbody> </table>			Method	296 °K	77 °K	Faraday rotation	3.77 eV 3.62 eV	3.79 eV 3.65 eV	Electroreflectance singularities	3.57 eV 3.80 eV		Absorption data	3.75 eV		Energy at which $\alpha \approx 10^6 \text{ m}^{-1}$	3.79 eV	
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Cyclotron resonance of semiconducting KTaO_3 at 70 GHz and 1.4 °K: microwave skin depth, about 30 μm ; see reference paper for the microwave absorption vs. magnetic field curves.																	
		67B1 65S13															

Tab. 11. KTaO_3 . Transverse optical modes at various temperatures [67P4]. The wave number $\tilde{\nu}_{t1}$ (ferroelectric soft mode) is temperature dependent.

$T [^\circ\text{K}]$	$\tilde{\nu}_{t1}$	$\tilde{\nu}_{t2}$	$\tilde{\nu}_{t3}$
	$\cdot 10^3 \text{ m}^{-1}$		
12	25	196	—
126	58	198	551
232	79	198	551
295	88	199	550
463	106	199	—

Tab. 12. KTaO_3 (Ca-doped). Singularities observed in electroreflectance spectra (in eV) [67F4]. See Figs. 40, 41

	E_1	E_2	A_1	A'_1	A_2
	[eV]				
KTaO_3 (100)	3.57	3.80	4.40	4.88	5.50
KTaO_3 (111)	—	3.77	4.45	4.90	5.47
KTaO_3 (110)	3.55	3.80	4.47	4.85	5.50

Tab. 13. KTaO_3 (reduced). Hall coefficient R_H and Hall mobility μ_H at 295 °K and 4.2 °K for single crystals [65W2]. Carrier concentrations N are calculated from the 4.2 °K Hall coefficient using $R_H = -1/Ne$

Sample Nr.	N_{calc} m^{-3}	R_H $\text{m}^2 \text{ C}^{-1}$		μ_H $\text{m}^2 \text{ V}^{-1} \text{ sec}^{-1}$	
		(295°K)	(4.2°K)	(295°K)	(4.2°K)
1	$3.5 \cdot 10^{23}$	$20.3 \cdot 10^{-6}$	$18 \cdot 10^{-6}$	$2.7 \cdot 10^{-3}$	2.3
2	$6.0 \cdot 10^{23}$	$12.9 \cdot 10^{-6}$	$10.4 \cdot 10^{-6}$	$2.9 \cdot 10^{-3}$	1.9
3	$6.6 \cdot 10^{23}$	$11.5 \cdot 10^{-6}$	$9.4 \cdot 10^{-6}$	$3.1 \cdot 10^{-3}$	1.9
4	$2.4 \cdot 10^{24}$	$3.0 \cdot 10^{-6}$	$2.6 \cdot 10^{-6}$	$3.0 \cdot 10^{-3}$	1.1
5	$7.8 \cdot 10^{24}$	$1.0 \cdot 10^{-6}$	$0.80 \cdot 10^{-6}$	$3.0 \cdot 10^{-3}$	0.53
6	$1.3 \cdot 10^{25}$	$0.62 \cdot 10^{-6}$	$0.48 \cdot 10^{-6}$	$3.1 \cdot 10^{-3}$	0.34

Tab. 14. KTaO_3 . Parameters of ESR spectrum of Eu^{2+} and Gd^{3+} ions, doped in single crystals of KTaO_3 [66U1]

Tab. 14. KLaO_3 . Parameters for KLaO_3 [6607]

Para-magnetic center	Site	S	\mathcal{H}	ν GHz	T °K	g-factor	FS	HFS	
							b_{40}, b_{60} 10^{-2} m^{-1}	I	A 10^{-2} m^{-1}
Eu^{2+}	K^+	7/2	(8)	9.1	77	1.990 ± 0.002	$b_{40} = (\pm)16 \pm 2$ $b_{60} = (\pm)1.2 \pm 0.6$	5/2 5/2	$ ^{151}\text{A} = 36 \pm 1$ $ ^{153}\text{A} = 16 \pm 1$
Gd^{3+}		7/2			4.2	1.990 ± 0.002	$b_{40} = -8.14 \pm 0.27$ $b_{60} = +0.47 \pm 0.3$		
					77	1.990 ± 0.002	$b_{40} = -7.0 \pm 0.3$ $b_{60} = +0.5 \pm 0.5$		

Tab. 15. KTaO_3 . Phonon energies of the soft ferroelectric mode (transverse optical mode) at various temperatures [67S1f]. The wave vector q at the zone boundary is 0.788 \AA^{-1} ($= \pi/a$). See Fig. 52

T °K	Phonon energy [meV] for $q [\text{\AA}^{-1}] =$		
	0	0.1	0.2
295	10.7	11.5	13.5
230	9.7		
170	8.6	10.0	12.5
120	7.3		
77	5.7	7.5	10.7
40	4.2	6.0	
28	3.6	5.9	10.5
15	3.0	5.3	
10	3.2	5.2	
4	3.1	5.3	9.8

Nr. 1A-5 CaTiO_3 , Calcium titanate (Perovskite)Tab. 16. CaTiO_3 . Ion positions. [57K2]

4 Ti in 4(a):	$\frac{1}{2}, 0, 0; 0, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, 0; 0, \frac{1}{2}, \frac{1}{2}$.
4 Ca in 4(c):	$x, \frac{1}{2}, z; \bar{x}, \frac{1}{2}, \bar{z}; \frac{1}{2} + x, \frac{1}{2}, \frac{1}{2} - z; \frac{1}{2} - x, \frac{1}{2}, \frac{1}{2} + z;$ with $x = 0, z = 0.030$.
4 O in 4(c):	with $x = \frac{1}{2} - 0.037, z = -0.018$.
8 O in 8(d):	$x, y, z; \frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z;$ $\bar{x}, \frac{1}{2} + y, \bar{z}; \frac{1}{2} + x, \bar{y}, \frac{1}{2} - z;$ $\bar{x}, \bar{y}, \bar{z}; \frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} - z;$ $x, \frac{1}{2} - y, z; \frac{1}{2} - x, y, \frac{1}{2} + z;$ with $x = \frac{1}{4} - 0.018, y = -0.026, z = \frac{1}{4} - 0.018$.

1a Specific heat anomaly associated with a phase transition was observed in CaTiO_3 at about 1260°C by NAYLOR et al. in 1946. GRÄNICHER et al. reported that CaTiO_3 becomes cubic above 1260°C .

b	phase	II	I
	state		P
	crystal system	orthorhombic	cubic
	space group	Pcmn-D_{2h}^{16}	

$\Theta \approx 1260^\circ\text{C}$

$\rho = 4.10 \cdot 10^3 \text{ kg m}^{-3}$ at RT.

$T_{\text{melt}} = 1960^\circ\text{C}$

$a = 5.3670 \text{ \AA}, b = 7.6438 \text{ \AA}, c = 5.4439 \text{ \AA}$ at RT.

The ideal perovskite cubic unit cell becomes pseudo-monoclinic in phase II in the same manner as shown in Fig. 21. $\beta' = 90^\circ 48'$ at RT.

Transparent, colorless.

2 Flux method; flux: $\text{CaCl}_2, \text{BaCl}_2, \text{CaCl}_2 + \text{BaCl}_2, \text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$.
Flame fusion method:

3 Crystal structure: $Z = 4$ in phase II.
Fig. 55; Tab. 16.

4 Lattice distortion: Fig. 56.

5a Dielectric constant: $\kappa = 186, \tan \delta = 3 \cdot 10^{-4}$ at RT.
Fig. 57.

6a Specific heat: Fig. 58.
Transition heat: $\Delta Q = 550 \text{ cal mol}^{-1}$ at $\Theta_{\text{II-I}}$.

46N1, 54G1

54G1

57K2

46N1

62M3

62M3

57K2

57K2
58L1, 62M3

57K2

62M3

46N1

9a	Nr. 1A-5 CaTiO ₃ , continued Refractive indices: Fig. 59. Reflection and absorption: Fig. 60, 61.			
17	Hardness: Mohs 6.5 ... 7, Knoop 986			62M3
Nr. 1A-6 SrTiO ₃ , Strontium titanate				
1a	Ferroelectric-like behavior of SrTiO ₃ was first observed by GRÄNICHER in 1956.			56G2
b	phase	II*	I	62R1
	state	(F)	P	
	crystal system	tetragonal	cubic**	
	space group		Pm3m-O _h ¹	
	Θ	110	°K	
	T _{melt} ≈ 2000 °C. ρ = 5.11 · 10 ³ kg m ⁻³ . a = 3.905 Å at RT. Transparent, colorless			63f2, 64l1 63f2 64L4
2a	Crystal growth: Flux method (flux: KF or 50% Na ₂ CO ₃ + 50% K ₂ CO ₃). Flame-fusion (Verneuil) method. Phase diagram of the system SrO-TiO ₂ is given in Figs. 297 and 289 of [64l1].			57N1 61G1 64l1
3	Crystal structure: Z = 1. Fig. 62.			
4	Thermal expansion: Fig. 63.			
5a	Dielectric constant: Figs. 64 ... 76. Expression of κ vs. T curve: Curie-Weiss law: κ = C/(T - Θ _p), T > 70 °K, where C = 7.83 · 10 ⁴ °K, Θ _p = 28 °K κ = M/[(T ₁ /2) coth(T ₁ /2T) - T ₀], T < 50 °K, where T ₀ = 38 °K, T ₁ = 84 °K, M = 9 · 10 ⁴ °K.			61M3 59W2, 62S2
b	Coefficients of free energy expansion at low temperatures:			66C6
c	Saturation polarization: Fig. 77. Remanent polarization: Fig. 78.			
d	Electrocaloric effect: Fig. 79. For additional data, see			64K5, 65H4, 61H1
6a	Specific heat: Fig. 80. Specific heat below 1 °K, see			61g1, 66A4
b	Thermal conductivity: Figs. 81, 82. For ceramics: see also			58Y1, 60Y1, 61g1, 66H9
7a	Piezoelectricity (dc bias induced piezoelectricity): Figs. 83, 84, 85.			
b	Electrostriction: Fig. 86.			
8a	Elastic compliances and stiffnesses: Tab. 17; Figs. 87, 88, 89.			
9a	Refractive indices: Tabs. 18, 19; Fig. 90. Reflectivity, absorption coefficient and dielectric constant: (i) Infrared region: Figs. 91 ... 95. See also Tab. 42. (ii) Visible and ultraviolet region: Figs. 96 ... 102. See also Tab. 43.			
b	Quadratic electrooptic effect: M ₁₁ - M ₁₂ = (0.14 ± 0.01) m ⁴ C ⁻² at 6328 Å (4.2 ... 300 °K).			64G3
c	Piezooptic effect: Tabs. 20, 21.			

* In phase II a hysteresis loop is observed,^{a)} b) but the remanent polarization depends upon the amplitude of the applied field. According to LYTLE, phase II consists of three phases. ^{a)} [59W2], ^{b)} [61M3], [64L4]

** Generally the phase I is believed to be cubic but evidence of pseudo-cubic structure was reported by a few authors. [64L4], [66C6]

9d	Nr. 1A-6 SrTiO ₃ continued	67B1
e	Faraday rotation: Fig. 103. See also Tab. 44. Raman effect: Fig. 104. Brillouin scattering: Fig. 105. See	66K1
10	Electrical resistivity: $\rho > 10^7 \Omega\text{m}$ (good quality single crystal) at RT. Fig. 106. For additional data, see Tab. 22. Resistivity, Hall coefficient and Hall mobility of semiconductive samples: Tab. 23; Figs. 107 ... 110. For additional data, see Hall mobility for photo-excited electron: see Fig. 115. Piezoresistivity: Figs. 111, 112, 113. Photoconductivity: Figs. 114, 115. Photoemission: Fig. 116. Superconductivity: discovered in semiconductive SrTiO ₃ by SCHOOLEY et al. in 1964. Figs. 117 ... 120. Tab. 24. Penetration depth of static magnetic field in superconductive SrTiO ₃ is of the order of 10^{-5} m.	61g1 61g1 64F5, 67T6 66T10 64S5 66S16
11	Magnetic susceptibility: Tab. 25.	
12a	NMR: Fig. 121.	
b	ESR: Tab. 26; Figs. 122 ... 130.	
c	Mössbauer effect: Figs. 131, 132.	
13c	Inelastic neutron scattering: Tab. 27; Figs. 133, 134, 135.	
14a	Domain structure: A fine twin structure was observed in phase II. The appearance of the twin structure is similar to that of the 90° domains in tetragonal BaTiO ₃ . The dc field, however, does not change the twin structure.	61M3, 64L4
16	Radiation damage: Fig. 136.	66R6
17	Etching and chemical polishing: Band structure and related properties: The band structure was determined theoretically by KAHN et al: Fig. 137. For discussions, see Magnetoresistance, Shubnikov-deHaas effect. The conduction band consists of spheroids along [100] having 3 minima at X_s . The transverse and longitudinal effective electron mass: $m_t = 1.5 m_0 (\pm 15\%)$, $m_l = 6.0 m_0 (\pm 30\%)$.	64K1 65S18 66F3, 67F3 67F3

Tab. 17. SrTiO₃. Elastic constants at RT

s_{11}	s_{12}	s_{13}	c_{11}	c_{12}	c_{13}	Method	Note	Reference
$10^{-12} \text{ m}^2 \text{ N}^{-1}$			10^{11} N m^{-2}					
3.3	-0.74	8.4	3.48	1.01	1.19	composite-bar	c calculated from s	58p5
3.729	-0.909	8.091	3.181	1.025	1.236	pulse	s calculated from c	63B2
3.772 ± 0.023	-0.926 ± 0.010	8.233 ± 0.040	3.156 ± 0.027	1.027 ± 0.027	1.215 ± 0.006		s calculated from c	63W1

Tab. 18. SrTiO₃. n vs. λ at 21 °C. [57G1]

λ Å	n	λ Å	n	λ Å	n
4200	2.6050	5400	2.4386	6600	2.3771
4300	2.5810	5500	2.4312	6700	2.3737
4400	2.5585	5600	2.4245	6800	2.3703
4500	2.5394	5700	2.4182	6900	2.3674
4600	2.5236	5800	2.4122	7000	2.3645
4700	2.5101	5900	2.4069	7100	2.3617
4800	2.4970	6000	2.4019	7200	2.3590
4900	2.4846	6100	2.3971	7300	2.3564
5000	2.4734	6200	2.3928	7400	2.3538
5100	2.4636	6300	2.3886	7500	2.3514
5200	2.4548	6400	2.3846	7600	2.3490
5300	2.4464	6500	2.3807	7700	2.3468

Tab. 19. SrTiO₃. n vs. λ [65B9]

λ μm	n	λ μm	n
0.45	2.537	1.8	2.270
0.5	2.472	2.0	2.264
0.6	2.402	2.2	2.258
0.7	2.363	2.4	2.2524
0.8	2.340	2.6	2.2490
0.9	2.326	2.8	2.2395
1.0	2.315	3.0	2.2315
1.1	2.306	3.2	2.2236
1.2	2.299	3.4	2.2143
1.4	2.287	3.6	2.2058
1.6	2.279	3.8	2.1951

Tab. 20. SrTiO_3 . Π_{66} vs. λ at $(27 \pm 1)^\circ\text{C}$. [57G1]

λ Å	Π_{66} $10^{-13} \text{ m}^2 \text{ N}^{-1}$	λ Å	Π_{66} $10^{-13} \text{ m}^2 \text{ N}^{-1}$
4200	-3.69	6000	-4.92
4300	-3.74	6100	-4.99
4400	-3.78	6200	-5.05
4500	-3.99	6300	-5.12
4600	-3.965	6400	-5.13
4700	-4.13	6500	-5.18
4800	-4.09	6600	-5.22
4900	-4.22	6700	-5.29
5000	-4.33	6800	-5.52
5100	-4.32	6900	-5.48
5200	-4.41	7000	-5.555
5300	-4.51	7100	-5.62
5400	-4.59	7200	-5.77
5500	-4.575	7300	-5.73
5600	-4.62	7400	-5.78
5700	-4.69	7500	-5.79
5800	-4.79	7600	-5.825
5900	-4.85	7700	-5.98

Tab. 21. SrTiO_3 . $\Pi_{21} - \Pi_{11}$ vs. λ at $(27 \pm 1)^\circ\text{C}$. [57G1]

λ Å	$\Pi_{21} - \Pi_{11}$ $10^{-13} \text{ m}^2 \text{ N}^{-1}$	λ Å	$\Pi_{21} - \Pi_{11}$ $10^{-13} \text{ m}^2 \text{ N}^{-1}$
4200	9.03	6000	9.95
4300	9.23	6100	9.94
4400	9.03	6200	9.91
4500	9.26	6300	9.84
4600	9.12	6400	9.82
4700	9.12	6500	9.88
4800	9.14	6600	9.96
4900	9.16	6700	9.92
5000	9.35	6800	9.98
5100	9.44	6900	9.99
5200	9.61	7000	9.91
5300	9.54	7100	9.92
5400	9.68	7200	9.94
5500	9.56	7300	9.99
5600	9.85	7400	10.05
5700	9.85	7500	9.90
5800	9.86	7600	9.92
5900	9.88	7700	10.02

Tab. 22. SrTiO_3 (single crystal). Effects of electrode material on the apparent conductivity [65C6]. Measurements were made by the two terminal method at $T = 130^\circ\text{C}$, $t = 24$ hours after the application of the field $E = 100 \text{ kV m}^{-1}$

Electrode material	σ [$\Omega^{-1} \text{ m}^{-1}$] after 24 h at 130°C	Form of σ vs. t curve
Au	$4.8 \cdot 10^{-7}$	Fall then rise
Ag	$8.8 \cdot 10^{-8}$	As for gold
Sn	$8.8 \cdot 10^{-9}$	Fall followed by slow rise but without saturation
Cr	$6.0 \cdot 10^{-11}$	Continuous fall tending toward steady value
Cd	$9.5 \cdot 10^{-11}$	Similar to chromium
Al	$2.9 \cdot 10^{-10}$	Similar to chromium (for a field of 400 kV m^{-1} behavior is like that of gold)

Tab. 23. SrTiO_3 (single crystal). The 300°K and 2°K Hall coefficient R_H and Hall mobility μ_H values and the 300°K electron concentrations for semiconductive single crystals. [67T6]. In the first column, (Nb) means Nb-doped samples, the other samples are reduced ones

Sample	300°K		2°K		$n = \frac{1}{eR_H(300^\circ\text{K})}$ m^{-3}
	R_H $10^{-6} \text{ m}^3 \text{ C}^{-1}$	μ_H $10^{-4} \text{ m}^2 \text{ V}^{-1} \text{ sec}^{-1}$	R_H $10^{-6} \text{ m}^3 \text{ C}^{-1}$	μ_H $10^{-1} \text{ m}^2 \text{ V}^{-1} \text{ sec}^{-1}$	
5	0.26	6.5	0.25	1.0	$2.4 \cdot 10^{25}$
2	0.62	5.2	0.77	1.8	$1.0 \cdot 10^{25}$
3	1.8	7.2	3.9	2.7	$3.5 \cdot 10^{24}$
6	5.3	8.0	11.0	3.1	$1.2 \cdot 10^{24}$
12	14.0	8.0			$4.5 \cdot 10^{23}$
9	23.0	5.8			$2.7 \cdot 10^{23}$
13(Nb)	0.22	5.5	0.22	3.3	$2.8 \cdot 10^{25}$
8(Nb)	0.58	4.8	0.63	8.2	$1.1 \cdot 10^{25}$
10(Nb)	3.4	6.2	3.3	12.0	$1.8 \cdot 10^{24}$
14(Nb)	14.0	6.7	11.0	13.0	$4.5 \cdot 10^{23}$
15(Nb)	22.0	5.4	18.0	19.0	$2.8 \cdot 10^{23}$
11(Nb)	44.0	6.0	33.0	22.0	$1.4 \cdot 10^{23}$

Tab. 24 see page 50

Tab. 25. SrTiO₃. Susceptibility in pure and reduced single crystals [66F7].

$\Delta\chi_{\text{mag}}$ represents the contribution from the charge carriers; χ_{mag} is obtained by measuring the χ_{mag} of reduced crystals and subtracting the "pure" diamagnetic and Van Vleck contributions, N = carrier concentration; T_{deg} = degeneracy temperature; m^* = density-of-state effective mass

Sample	N at 4.2 °K m^{-3}	T_{deg} °K	χ_{mag} or $\Delta\chi_{\text{mag}} \cdot 10^{-7} \text{ cm}^3 \text{ g}^{-1}$		m^* at 4.2 °K [m_0]
			300 °K	78 °K	
pure 28 h, 950 °C hydrogen 5 h, 1200 °C hydrogen (carbon boat) reoxidized 18 h, 700 °C, air	$6 \cdot 10^{24}$ $7.5 \cdot 10^{25}$	28 148	-1.02	-1.00	-
			+0.037	+0.073	-
			+0.270	+0.523	5.1
			-	-	-
27 h, 1370 °C hydrogen (carbon boat)	$5.3 \cdot 10^{26}$	550	-1.016	-1.012	-
			+1.704	+1.763	4.9

Tab. 27. SrTiO₃. The frequency of the lowest transverse optic mode at $q = 0$ for five different temperatures. [62C4]

T °K	10^{12} sec^{-1}	
	Neutron	Far infrared
90	1.23 ± 0.03	$1.2^a)$
142	1.72 ± 0.04	
203	2.24 ± 0.05	
296	2.73 ± 0.05	
430	3.32 ± 0.07	$3.0^a)$ $2.63^b)$

a) [62B2] b) [62S12]

Tab. 26. SrTiO₃. Summary of the properties of ESR spectrum in SrTiO₃ for various doped paramagnetic ions

Para-magnetic center	Site	S	\mathcal{H}	ν GHz	T °K	g -factor		FS D, E, a [10^{-2} m^{-1}]	I	HFS		Ref.	Literature
						g_{\parallel}	g_{\perp}			aA [10^{-2} m^{-1}]	bA [10^{-2} m^{-1}]		
Cr ³⁺	Ti ⁴⁺	3/2	(5)	9	80	1.9788 ± 0.007	(isotropic)	$D = 2 \pm 0.3, E = 0$	3/2	$aA = 0$		f)	58M7
					300	1.9780 ± 0.007	(isotropic)	$D = 0, E = 0$		$aA = 16.2 \pm 0.3$			62M6
Mn ²⁺	Ti ⁴⁺	3/2	(5)	10	77	1.994 ± 0.001	(isotropic)	$D = +1.0, E = 0$	5/2	$aA = -69.4 \pm 1$			59M4
					RT	1.994 ± 0.001	(isotropic)	$D = -0.7, E = 0$		$aA = -69.4 \pm 1$		a) b) c) d) e)	59D2
Fe ³⁺	Ti ⁴⁺	5/2	(7)	9	1.9	2.004 ± 0.001	(isotropic)	$D = +17.9 \pm 1.0, E = 0$					58M8
					4.2	2.004 ± 0.001	(isotropic)	$a = -230 \pm 10, E = 0$					
Ni ²⁺	Ti ⁴⁺	1	(4)	10	77	2.004 ± 0.001	(isotropic)	$D = +16.1 \pm 0.7, E = 0$					
					300	2.004 ± 0.001	(isotropic)	$a = -225.6 \pm 1.9$					
Ni ¹⁺ or Ni ³⁺	Ti ⁴⁺	1/2	(2)	10	80	2.004 ± 0.001	(isotropic)	$D = +7.3 \pm 0.3, E = 0$					
					20	2.004 ± 0.001	(isotropic)	$a = -220.8 \pm 1.1$					
					80	2.029 ± 0.001	(isotropic)	$D = 1.0, E = 0$					
					203	2.029 ± 0.001	(isotropic)	$a = -197.7 \pm 0.7$					

Ni ³⁺	Ti ⁴⁺	1	(4)	10	20	2.352 ± 0.001	9)
Ni ³⁺ or Ni ³⁺	Ti ⁴⁺	1/2	(2)	10	80	2.029 ± 0.001	
				203			

Para-magnetic center	Site	S	J	ν GHz	T °K	g-factor		FS D, E, a [10 ⁻³ m ⁻¹]	HFS I ^a A , ^a A _⊥ [10 ⁻³ m ⁻¹]	Ref.	Literature
						g	g _⊥				
Ni ³⁺	Ti ⁴⁺	1/2	(2)	10	4.2	2.110 ± 0.002	2.213 ± 0.002			9)	62R3
					20	2.136 ± 0.001	2.202 ± 0.001				
					80	2.172 ± 0.001	2.184 ± 0.001				
					203	(isotropic)	2.180 ± 0.002				
Ca ³⁺	—	1/2	(2)	10	4.2	3.005 ± 0.005	1.118 ± 0.003			9)	62R3
					4.2	2.609 ± 0.003	2.472 ± 0.003				
Nd ³⁺	—	1/2	(2)	16	2	2.61 ± 0.01	2.470 ± 0.005			9)	62R2
					35	2.62 ± 0.01	2.470 ± 0.005				
					16	2.11 ± 0.01	2.780 ± 0.005				
Yb ³⁺	—	1/2	(3)	35	2	2.10 ± 0.005					62R2
					50	2.18 ± 0.01	2.720 ± 0.005		1/2 ¹⁷¹ A = 530 ± 20 ¹⁷¹ A _⊥ = 720 ± 5		
					65	(2.25)	2.70 ± 0.01		5/2 ¹⁷³ A _⊥ = 211 ± 5		
Eu ³⁺	—	7/2	(8)	16	2	1.99 ± 0.001	-10 ± 4	b ₄₀ 6.7 ± 2	5/2 ¹⁸¹ A = 36.2 ¹⁸³ A _⊥ = 17.6	f)	62R2
					300	1.99 ± 0.001	0	b ₄₀ 1.1 ± 2			
					2	1.992 ± 0.002	-362.5 ± 0.5	1.4 ± 0.5			
Gd ³⁺	Sr ³⁺	7/2	(8)	12, 18	4.2	1.992 ± 0.002	-362.5 ± 0.5	1.4 ± 0.5		f) b)	62R2 62R1
					77	1.992 ± 0.002	-233.6 ± 0.5	-0.25 ± 0.5			
					300	1.992 ± 0.002	-5.7 ± 0.2	0.5 ± 0.3			

a) ξ = [100], η = [010], ζ = [001].

b) Deviations from spin Hamiltonian (7) is ascribed to a covalent bonding by MÜLLER. However, AISENBERG et al. find a negligible contribution of the covalent bonding. [59A].

c) Spectrum is due to a double quantum absorption between S_g = -1 and S_g = +1 levels.

d) At least fifteen inequivalent sites are observed.

e) Three inequivalent spectra are observed with axes parallel to the cubic [100], [010] and [001].

f) Effects of temperature and pressure on Cr³⁺, Fe³⁺, Eu³⁺, and Gd³⁺ spectra. [64R2].g) Fe³⁺ spectra due to nearest charge compensation. [64K7].h) Electric field dependence of Gd³⁺ spectra. [66S7].

Tab. 24. SrTiO_3 (ceramics containing Ba or Ca in mol%). Superconductive properties of $(\text{Ba}_x\text{Sr}_{1-x})\text{TiO}_3$ and $(\text{Ca}_x\text{Sr}_{1-x})\text{TiO}_3$ [67S8]. H_{c1} is the point at which the magnetization curve first deviates from linearity; $H_{c1}(0)$ is the extrapolated value for $T \rightarrow 0^\circ\text{K}$.
 N = Carrier concentration Θ_c = superconducting transition temperature

% Ba or Ca	N 10^{25} m^{-3}	Θ_c $^\circ\text{K}$	$H_{c1}(0)$ Oe	% Ba or Ca	N 10^{25} m^{-3}	Θ_c $^\circ\text{K}$	$H_{c1}(0)$ Oe
—	2.7	0.18		10.0	4.2	0.25	
—	5.8	0.30	2.8	12.5	4.5	<0.10	
—	6.4	0.25	2.8				
—	1.7	0.10		2.5 (Ca)	5.0	0.32	
—	12.0	0.17		5.0	9.2	0.30	
—	23.0	0.10		7.5	74.0	<0.06	
2.5 (Ba)	6.0	0.52		7.5	8.7	0.43	
2.5	0.3	0.23		7.5	0.2	<0.06	(3.5) ^{a)}
5.0	6.7	0.50		7.5	0.6	0.37	
7.5	7.0	0.29	3.9	7.5	33.0	<0.07	
7.5	0.05	0.22		7.5	2.0	0.48	
7.5	34.0	0.09		7.5	0.06 ^{b)}	<0.06	
7.5	0.5	0.25		10.0	9.3	0.39	
7.5	2.3	0.27		20.0	13.0	0.29	
7.5	15.0	0.45		30.0	6.7	0.50	1.9
				30.0	0.6	<0.05	

Nr. 1A-7 CdTiO_3 , Cadmium titanate

1a	CdTiO ₃ was reported by SMOLENSKII in 1950 to be ferroelectric below 50 ... 60 °K. In 1950 HULM et al. denied its ferroelectricity but HEGENBARTH supported SMOLENSKII's findings.			50S7, 50H2, 59H4
b	phase	II	I	
	state	(F) ^{a)}		
	crystal system		orthorhombic ^{b)}	a) 50S7
	space group		Pc2 ₁ n ^{b)} -C _{2v} ^{b)}	b) 57K1
	Θ	-223... -213 °C		
	Lattice constants: a = 5.348 Å, b = 7.615 Å, c = 5.417 Å at RT. The relation between the orthorhombic unit cell and the pseudo-cubic monoclinic cell is the same as in the case of NaTaO ₃ ; see Fig. 21.			50S7 57K1
2	Flux method (flux: 40 wt% NaCl + 40 wt% NaBO ₂ + 20 wt% Na ₂ CO ₃).			
3	Z = 4. Crystal structure in phase I: Tab. 28; Fig. 138.			57K1
5a	Dielectric constant: κ = 250 at RT. κ = C/(T - Θ _p), C = 4.5 · 10 ⁴ °K.			
b	Effect of E _{bias} on κ: Fig. 139.			50S7, 50H2

		Positions				Estimated error
Tab. 28. CdTiO_3 . Fractional coordinates of atoms in the unit cell. [57K1]						
Cd	x :	$0 + 0.006$	$0 - 0.006$	$\frac{1}{2} + 0.006$	$\frac{1}{2} - 0.006$	± 0.002
	y :	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	
	z :	$0 + 0.016$	$0 - 0.016$	$\frac{1}{2} - 0.016$	$\frac{1}{2} + 0.016$	± 0.002
Ti	x :	$\frac{1}{2} + 0.005$	$\frac{1}{2} - 0.005$	$0 + 0.005$	$0 - 0.005$	± 0.005
	y :	0	$\frac{1}{2}$	$\frac{1}{2}$	0	
	z :	$0 - 0.065$	$0 + 0.065$	$\frac{1}{2} + 0.065$	$\frac{1}{2} - 0.065$	± 0.010
O(1)	x :	$0 - 0.03$	$0 + 0.03$	$\frac{1}{2} + 0.03$	$\frac{1}{2} - 0.03$	± 0.015
	y :	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	± 0.025
	z :	$\frac{1}{2} + 0.05$	$\frac{1}{2} - 0.05$	$0 + 0.05$	$0 - 0.05$	± 0.015
O(2)	x :	$\frac{1}{2} + 0.05$	$\frac{1}{2} - 0.05$	$\frac{1}{2} - 0.05$	$\frac{1}{2} + 0.05$	± 0.005
	y :	$0 - 0.03$	$0 - 0.03$	$\frac{1}{2} - 0.03$	$\frac{1}{2} - 0.03$	± 0.015
	z :	$\frac{1}{2} + 0.06$	$\frac{1}{2} + 0.06$	$\frac{1}{2} - 0.06$	$\frac{1}{2} - 0.06$	± 0.015
O(3)	x :	$\frac{1}{2} + 0.05$	$\frac{1}{2} - 0.05$	$\frac{1}{2} - 0.05$	$\frac{1}{2} + 0.05$	± 0.005
	y :	$\frac{1}{2} + 0.07$	$\frac{1}{2} + 0.07$	$0 + 0.07$	$0 + 0.07$	± 0.015
	z :	$\frac{1}{2} + 0.06$	$\frac{1}{2} + 0.06$	$\frac{1}{2} - 0.06$	$\frac{1}{2} - 0.06$	± 0.015

^{a)} This specimen is not spherical, so that the value of $H_{c1}(0)$ quoted is only approximate.
^{b)} Hall coefficient appeared to be affected by magnetic history of specimen at liquid helium temperature.

Nr. 1A-8 BaTiO₃, Barium titanate

(Responsible authors for this section are as follows: IKEDA, NAKAMURA, NOMURA, SAWAGUCHI, SHIOZAKI and TOYODA, abbreviated as INaNoSaShiTo).

1a	The anomalous dielectric properties of BaTiO ₃ were discovered on ceramic specimens independently by WAINER and SOLOMON in 1942, by OGAWA in 1944 and by WUL in 1945. The ferroelectric activity of BaTiO ₃ was reported independently by VON HIPPEL and co-workers in 1944 and by WUL in 1946. The structural change associated with the cubic-tetragonal phase transition was observed, by means of x-rays, by MEGAW in 1945, independently of the above dielectric studies.					42W1, 44O1, 45W1, 44V2, 46W2, 45M1
b	phase	IV ^{a)}	III ^{a)}	II ^{b)}	I ^{b)}	^{a)} 49K2, 49R1
	state	F ^{a)}	F ^{a)}	F ^{c)}	P ^{b)}	^{b)} 45M1
	crystal system	rhombic ^{a)}	ortho-rhombic ^{a)}	tetragonal ^{b)}	cubic ^{b)}	^{c)} 46V1, 46W1
	space group	R3m-C _{3v} ^{a)}	Amm2-C _{2v} ^{a)}	P4mm-C _{4v} ^{b)}	Pm3m-O _h ^{b)}	^{d)} 55R1
	θ	-90 ^{a)}	5 ^{a)}	120 ^{b)} **	1460 ^{d)}	°C
	$P_a \parallel [001]$ in phase II (along $[100]$ of phase I). $P_a \parallel [001]$ in phase III (along $[110]$ of phase I). $P_a \parallel [111]$ in phase IV (along $[111]$ of phase I). The directions of P_a are illustrated along with lattice distortions in Fig. 140. $T_{\text{melt}} = 1618^\circ\text{C}$. Tetragonal form (phase II): $\rho = 6.02 \cdot 10^3 \text{ kg m}^{-3}$ (calculated from lattice constants) $a = 3.9920 \text{ \AA}$, $c = 4.0361 \text{ \AA}$ at 20°C . Transparent, light brown. Hexagonal form: $a_{\text{hex}} = 5.735 \text{ \AA}$, $c_{\text{hex}} = 14.05 \text{ \AA}$ at RT. $\rho = (6.1 \pm 0.1) \cdot 10^3 \text{ kg m}^{-3}$.					51W2, 51R1, 48B3
2a	Crystal growth: Flux method (flux KF ^{a)} or TiO ₂ -rich melt ^{b)}). Pulling method (top-seeded solution growth technique using excess TiO ₂ as the solvent). Melting method (with limited success). Tab. 29; Fig. 141.					^{a)} 54R1, ^{b)} 65S8
b	Crystal forms: For butterfly-type: Fig. 142. For chunky type: Fig. 143. For hexagonal form: Fig. 144.					63L3, 50V2
3	Crystal structure of phase I: $Z = 1$. Tab. 30. Crystal structure of phase II: $Z = 1$. Tab. 31. Crystal structure of phase III: $Z = 2$. Tab. 32; Fig. 145, 146; Tab. 33. Crystal structure of phase IV: $Z = 1$. Crystal structure of hexagonal form: $Z = 6$. Tab. 34, 35; Fig. 147.					
4	Lattice constants of phase I, II, III, and IV: Phase I: $a = 3.996 \text{ \AA}$ at 120°C . Phase II: $a = 3.9920 \text{ \AA}$, $c = 4.0361 \text{ \AA}$ at 20°C . Phase III: $a = 3.990 \text{ \AA}$, $b = 5.669 \text{ \AA}$, $c = 5.682 \text{ \AA}$ at -10°C . Phase IV: $a = 4.001 \text{ \AA}$, $\alpha = 89^\circ 51'$ at -168°C . Thermal expansion: Fig. 148, 149; Tab. 36, 37; Fig. 150. Lattice distortion due to p : Fig. 151.					47M3, 51R1, 57S2, 57J2
5a	Dielectric constant: Fig. 152, 153, 154, 192. Dielectric dispersion: Fig. 155 ... 159. Further data from optical measurements: Fig. 201; Tab. 42. Effect of p on κ : Fig. 160, 161, 162. Phase diagram in regard to p : Fig. 163, 164. Effect of E_{bias} on θ_f : $d\theta_f/dE_{\text{bias}} = 1.43 \cdot 10^{-5} \text{ }^\circ\text{K V}^{-1} \text{ m}$; on κ : Fig. 165.					53M2
b	Non-linear dielectric properties: Fig. 166. $\xi = -5.5 \cdot 10^8 \text{ J C}^{-4} \text{ m}^5$, $\zeta = 1.7 \cdot 10^{10} \text{ J C}^{-6} \text{ m}^9$.					53M2

* The transition from the hexagonal form to the cubic one is very sluggish and the hexagonal form can be produced by rapid cooling from above 1460°C .

** In most papers this Curie point has been reported to be about 120°C , but it seems to be about 130°C for pure BaTiO₃ [65J2].

5c	Nr. 1A-8 BaTiO ₃ continued Spontaneous polarization: Fig. 167, 168, 169. Coercive field: Fig. 170, 171, 172. Effect of p on P_s : Fig. 173.	
d	Electrocaloric effect: Fig. 174. Pyroelectricity: Fig. 175.	
6a	Specific heat: Fig. 176, 177. Transition heat, transition entropy: Tab. 38.	
b	Thermal conductivity: Fig. 178, 179.	
7a	Piezoelectricity: Tab. 39, 40; Fig. 180 ... 183.	
b	Electrostriction: Fig. 184, 185.	
8a	Elastic compliances and stiffnesses: Tab. 41. See also Tab. 40. Fig. 186 ... 193.	
b	Non-linear elastic properties: Fig. 194.	
9a	Refractive indices: Fig. 195, 196, 197. Birefringence: Fig. 198, 199. Reflection and absorption: (i) Far-infrared region. Fig. 200, 201; Tab. 42. (ii) Infrared region. Fig. 202, 203, 204. (iii) Visible region. Fig. 205, 206, 207. (iv) Ultraviolet region. Fig. 208; Tab. 43; Fig. 209, 210, 211. For the effect of E_{bias} on the absorption edge, see	67G1
b	Linear electrooptic effect: Fig. 212 ... 215. Quadratic electrooptic effect: $(M_{11} - M_{12}) = (+ 0.13 \pm 0.02) \text{ m}^4 \text{ C}^{-2}$ at 408 ... 433 °K, measured at 6328 Å.	64G3
d	Faraday rotation: Fig. 216; Tab. 44.	64M2
e	Non-linear optical properties: Susceptibility for SHG (second harmonic generation) (relative values, see Sec. IC): $d_{15} = 35 \pm 3$, $d_{31} = 37 \pm 3$, $d_{33} = 14 \pm 1$, determined with the Nd-doped CaWO ₄ laser beam. Fig. 217.	
f	Raman scattering: Fig. 218.	
g	Luminescence: Fig. 219, 220.	
10	Conductivity of as-grown crystals and ceramics: The data vary from sample to sample depending on the purity and the method of preparation: only representative data are given here. Fig. 221 ... 225. Conductivity associated with doping or reduction (including PTC (Positive Temperature Coefficient) or resistivity: $d\rho/dT > 0$): Fig. 226 ... 230. Reference papers on PTC anomaly: Tab. 45. Piezoresistivity: Fig. 231, 232. For additional data, see Breakdown strength: Fig. 233, 234. For additional data, see Photoconductivity and photoemission: Fig. 235, 236. Other transport properties: In n -type single-domain crystals, the electron mobility is anisotropic at RT; $\mu_{\perp c} \approx 1.2 \cdot 10^{-4} \text{ m}^2 \text{ V}^{-1} \text{ sec}^{-1}$, and $\mu_c \approx 0.13 \cdot 10^{-4} \text{ m}^2 \text{ V}^{-1} \text{ sec}^{-1}$ In n -type single-domain crystals, the energy separation ($\Delta u = 10^{-2} \dots 10^{-1} \text{ eV}$) between the c -axis conduction band minima and the a -axis conduction band minima has been estimated vs. T . In n -type single-domain crystals, the density-of-state mass $m^* = (6.5 \pm 2) m_0$. Data are available on the Hall coefficient and conductivity of single domain crystals having donor concentrations of $N = 8.5 \cdot 10^{24} \text{ m}^{-3}$ and of $N = 2.5 \cdot 10^{23} \text{ m}^{-3}$. Fig. 237. Seebeck-effect: Fig. 238.	59S1, 63M1, 67G4 58I3, 59F1, 64K3, 64U1 67B2 67B2 67B2 67B2
12b	ESR: Tab. 46; Fig. 239 ... 243.	
c	Mössbauer effect: Fig. 244 ... 247.	
13b	Diffuse X-ray scattering: Fig. 248, 249, 250. Inelastic neutron scattering: Fig. 251.	

14a	Domain structure: Domains have been observed by various methods: polarized light ^{a)} , X-rays ^{b)} , electron microscope ^{c)} , etching method ^{d)} , powder pattern method ^{e)} , and decoration method ^{f)} . Fig. 252 ... 255.	a) 48M1, 49F1, 52M3 b) 63B13, 64N1, 65C3, 64L1 c) 62T1, 63B9, 67R4, 64T2, 66R5, 67R2 d) 55H2 e) 59P1 f) 66S8
b	Domain wall motion: Domain wall motion has been observed optically ^{a)} and by repeated differential etching ^{b)} . The domain shapes in motion depend on the applied field and temperature. ^{c)} Fig. 256. The wall velocity is proportional to $\exp(-\delta/E)$ at relatively low field. δ = activation field for domain wall motion. Fig. 257 ... 267.	a) 59M2, 60S2 b) 63S13 c) 63S13 58M4, 59M3
15	Surface layer: The first suggestion about the existence of surface layers of BaTiO ₃ crystals was made by KÄNZIG ^{a)} on the basis of electron diffraction studies of very small particles of BaTiO ₃ ^{b)} . The dependence of the following quantities on the thickness of the crystals has been observed as evidence of the existence of surface layers: domain wall velocity ^{c)} , dielectric constant ^{d)} , optical absorption coefficient ^{e)} and electroluminescence spectra ^{f)} . Pyroelectric current was observed above the Curie point and discussed in connection with surface layers ^{g)} . A few models of surface layers have been proposed ^{h)} . According to TANAKA and HONJŌ ⁱ⁾ , the surface layer, if it exists, seems to be very thin.	a) 55K1 b) 54A1 c) 56M4, 61M2, 65C1 d) 61S4, 62C3 e) 60C3 f) 58H1, 65B7, 66B6 g) 56C1 h) 56M4, 61F2, 59D3, 65C1 i) 64T2
16	Radiation damage: Fig. 268, 269.	
17	Energy band structure: Fig. 270.	

Tab. 29. BaTiO₃. Solubility in KF solution. [54K1]

T	1000	1050	1100	1150	1200	1250	1300	°C
BaTiO ₃	4	6	9	12.5	17	22.5	28.5	mole %

Tab. 30. BaTiO₃. Fractional coordinates of atoms in the unit cell of phase I. [52M2]

	x	y	z
Ba	0	0	0
Ti	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
O	$\frac{1}{2}$	$\frac{1}{2}$	0
	$\frac{1}{2}$	0	$\frac{1}{2}$
	0	$\frac{1}{2}$	$\frac{1}{2}$

Tab. 31. BaTiO₃. Shift of atoms in fractional coordinates of phase II from the positions of phase I. [51K1], [55F1], [61E3]

δz_{Ti}	$\delta z_{O(1)}$	$\delta z_{O(2)}$	Ba		Ti		O(1)		O(2)			References
			B ₁₁	B ₃₃	B ₁₁	B ₃₃	B ₁₁	B ₂₂	B ₁₁	B ₂₂	B ₃₃	
0.014	-0.032	0	0.48		0.13		0.13		0.48			51K1
0.014	-0.023	-0.014	0.273		0.152		0.334		0.267			55F1
0.015	-0.024	-0.020	0.27	0.28	0.53	0.21	0.90	0.08	0.60	0.49	0.07	61E3
0.012	-0.026	0	0.27	0.28	0.46	0.30	0.90	0.50	0.60	0.90	0.90	61E3

The positions of atoms in the unit cell are Ba at (0, 0, 0), Ti at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2} + \delta z_{Ti}$), O(1) at ($\frac{1}{2}$, $\frac{1}{2}$, $\delta z_{O(1)}$) and O(2) at ($\frac{1}{2}$, 0, $\frac{1}{2} + \delta z_{O(2)}$).

Tab. 32. BaTiO₃. Fractional coordinates of atoms in the unit cell of phase III. [57S2]

	x	y	z
Ba	0	0	0
Ti	0	$\frac{1}{2}$	$\frac{1}{2}$
O(1)	$\frac{1}{2}$	0	$\frac{1}{2} + \delta z_{Ti}$
	$\frac{1}{2}$	$\frac{1}{2}$	δz_{Ti}
	0	0	$\frac{1}{2} + \delta z_{O(1)}$
	0	$\frac{1}{2}$	$\delta z_{O(1)}$
O(2)	$\frac{1}{2}$	$\frac{1}{2} + \delta y_{O(2)}$	$\frac{1}{2} + \delta z_{O(2)}$
	$\frac{1}{2}$	$\frac{1}{2} + \delta y_{O(2)}$	$\frac{1}{2} + \delta z_{O(2)}$
	$\frac{1}{2}$	$\frac{1}{2} - \delta y_{O(2)}$	$\frac{1}{2} + \delta z_{O(2)}$
	$\frac{1}{2}$	$\frac{1}{2} - \delta y_{O(2)}$	$\frac{1}{2} + \delta z_{O(2)}$

$$\delta z_{Ti} = +0.010; \delta z_{O(1)} = -0.010; \delta z_{O(2)} = -0.013; \delta y_{O(2)} = +0.003.$$

Tab. 33. BaTiO₃. Comparison of atomic shifts in phase III and phase II with respect to different origins. The coordinate of atoms of [55F1] and [57S2] are used for phase II and III, respectively. [57S2]

	Orthorhombic	Tetragonal
Ba at (000)		
δz { Ti	+0.06 Å	+0.06 Å
O(1)	-0.06 Å	-0.09 Å
O(2)	-0.07 Å	-0.06 Å
$\delta y_{O(2)}$	± 0.02 Å	—
Origin is chosen to give $\delta z_{O(2)} = 0$		
δz { Ti	+0.13 Å	+0.15 Å
Ba	+0.07 Å	+0.09 Å
O(1)	+0.02 Å	-0.03 Å

Tab. 34. BaTiO₃. Fractional coordinates of atoms in the unit cell of hexagonal structure. [48B3]

2Ba(1) at (b),	
4Ba(2) at (f),	$z = 0.097$,
2Ti(1) at (a),	
4Ti(2) at (f),	$z = 0.845$,
6O(1) at (h),	$z = 0.522$,
12O(2) at (k),	$z = 0.836, z = 0.076$

Tab. 35. BaTiO₃. Interatomic distances of hexagonal structure. [48B3]

in the Ti ₂ O ₇ group	
O(1) — O(1) = 2.49 Å	in the shared face.
= 3.25 Å	
O(2) — O(2) = 2.91 Å	in the same layer but the atoms do not belong to the same shared face.
O(1) — O(2) = 2.91 Å	
Ti(2) — O(1) = 1.96 Å	
Ti(2) — O(2) = 2.02 Å	
in the TiO ₆ octahedra	
O(2) — O(2) = 2.82 Å	in the same layer.
O(2) — O(2) = 2.69 Å	
Ti(1) — O(2) = 1.95 Å	between adjacent layers.

Tab. 36. BaTiO₃. Lattice constants and unit cell volume at various T . [51R1]

T °C	a Å	b Å	c Å	V Å ³
+ 20	3.9920	3.9920	4.0361	64.317
+ 4	3.9910	3.9911	4.0357	64.282
Θ_{III-II}				
+ 4	4.0185	3.9860	4.0162	64.319
- 99	4.0170	3.9750	4.0150	64.093
Θ_{IV-III}				
- 99	4.0015	4.0015	4.0020	64.079
- 160	3.9996	3.9996	3.9997	63.981

Accuracy of measurement below RT was ± 0.0007 Å.

Tab. 37. BaTiO₃. Linear thermal expansion coefficients along a , b , and c axes. [51R1]

T °C	α_a $10^{-6} \text{ } ^\circ\text{C}^{-1}$	α_b $10^{-6} \text{ } ^\circ\text{C}^{-1}$	α_c $10^{-6} \text{ } ^\circ\text{C}^{-1}$
+20 ... + 4	15.7	15.7	6.2
+ 4 ... - 99	4.9	28.4	-0.9
-99 ... -160	7.8	7.8	8.2

Tab. 38. BaTiO₃. Transition heats and transition entropies

Transition	ΔQ_m cal mol ⁻¹	ΔS_m cal mol ⁻¹ °K ⁻¹	References
IV → III	8 ± 2	0.04	52S5
	14.3	0.07	52V1
	12	0.06	52T1
III → II	22 ± 4	0.076	52S5
	15.5	0.054	52V1
	16	0.058	52T1
II → I	50 ± 5	0.125	52S5
	47	0.12	52V1
	47	0.12	48B1

Tab. 39. BaTiO₃ (single crystal and ceramic). Piezoelectric constants and electromechanical coupling factor. [66b1]

	d_{15}	d_{31}	d_{33}	$10^{-12} \text{ C N}^{-1}$			k_p	10^8 N C^{-1}			T $^\circ\text{C}$	References
				g_{15}	g_{31}	g_{33}		e_{15}	e_{31}	e_{33}		
single crystal	392	—	—	15.3	-23.1	57.6	0.560				20	50C2
	—	57.7	132	—	—	—	—				25	58B2
	—	34.5	85.6	—	—	—	—				RT	59H7
ceramic	270	—	—	18.8	-4.7	11.4	0.378	11.6	-4.4	18.6	25	56B3
	260	—	—	20.2	-5.2	12.6	0.36	11.4	-4.35	17.5	25	64b1
	—	79	191	—	—	—	—					
	—	78	190	—	—	—	—					

Tab. 40. BaTiO₃ (ceramic, plain and modified, commercial). Dielectric, piezoelectric, electromechanical and elastic constants (at 25 $^\circ\text{C}$, except for Ca_{0.13}Pb_{0.08}Ba_{0.80}TiO₃). [66b1]

Composition	κ_{11}^I	κ_{11}^S	κ_{33}^S	$10^{-12} \text{ C N}^{-1}$			$10^{-8} \text{ m}^2 \text{ C}^{-1}$			k_p	$10^{-12} \text{ m}^2 \text{ N}^{-1}$			s_{66}
				d_{15}	d_{31}	d_{33}	g_{15}	g_{31}	g_{33}		k_{15}	k_{31}	k_{33}	
BaTiO ₃	1350...	—	—	—	—	—	—	—	—	—	—	—	—	—
Ca _{0.05} Ba _{0.95} TiO ₃	1700	—	—	—	—	—	—	—	—	—	—	—	—	—
Ca _{0.05} Ba _{0.95} TiO ₃	1380	—	—	—	—	—	—	—	—	—	—	—	—	—
Ca _{0.05} Ba _{0.95} TiO ₃	1200	—	—	—	—	—	—	—	—	—	—	—	—	—
(ceramic B) ^{a)}	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ca _{0.05} Ba _{0.95} TiO ₃	910	—	—	—	—	—	—	—	—	—	—	—	—	—
Pb _{0.04} Ba _{0.96} TiO ₃	1000	—	—	—	—	—	—	—	—	—	—	—	—	—
Pb _{0.04} Ba _{0.96} TiO ₃	1180	—	—	—	—	—	—	—	—	—	—	—	—	—
Ca _{0.05} Pb _{0.05} Ba _{0.90} TiO ₃	800	—	—	—	—	—	—	—	—	—	—	—	—	—
Ca _{0.05} Pb _{0.05} Ba _{0.90} TiO ₃	600	—	—	—	—	—	—	—	—	—	—	—	—	—
Ca _{0.05} Pb _{0.05} Ba _{0.90} TiO ₃	450	—	—	—	—	—	—	—	—	—	—	—	—	—
Ca _{0.13} Pb _{0.08} Ba _{0.80} TiO ₃	600	—	—	—	—	—	—	—	—	—	—	—	—	—
Ca _{0.05} Ba _{0.95} TiO ₃ (ceramics B) ^{a)}	κ_{11}^I	κ_{11}^S	κ_{33}^S	d_{15}	d_{31}	d_{33}	g_{15}	g_{31}	g_{33}	k_p	k_{15}	k_{31}	k_{33}	s_{66}
	1300	1000	910	10.9	—3.1	13.5	8.3	9.1	7.0	-2.7	-1.9	22.2	17.1	—
Ca _{0.05} Pb _{0.15} Ba _{0.80} TiO ₃	κ_{11}^I	κ_{11}^S	κ_{33}^S	d_{15}	d_{31}	d_{33}	g_{15}	g_{31}	g_{33}	k_p	k_{15}	k_{31}	k_{33}	s_{66}
	12.3	-3.8	16.7	15.8	159	150	177	69	70	67.5	62	45	58.5	45

^{a)} Trade Mark: Clevite Corporation, Cleveland, Ohio, USA.

Tab. 41. BaTiO₃ (single crystal and ceramics). Elastic constants. [66b1]

	$10^{-12} \text{ m}^2 \text{ N}^{-1}$											T °C	References
	s_{11}^E	s_{12}^E	s_{13}^E	s_{14}^E	s_{22}^E	s_{23}^E	s_{24}^E	s_{33}^E	s_{34}^E	s_{44}^E	s_{66}^E		
single crystal	9.26 11.2	7.25	15.7	10.8	-2.35	-3.15	-5.24	-3.26	18.4	12.4	8.84	25 RT	50C2 51B1 58B2
ceramics	8.55 9.1	8.18 8.7	8.93 9.5	6.76 7.1	-2.61 -2.7	-2.98 -3.0	-2.85 -2.9	-1.95 -1.9	23.3 22.8	18.3 17.5	22.3 23.6	25	56B3 64b1
	c_{11}^E	c_{12}^E	c_{13}^E	c_{14}^E	c_{22}^E	c_{23}^E	c_{24}^E	c_{33}^E	c_{34}^E	c_{44}^E	c_{66}^E	25	
single crystal	275.1	282.6 206	164.9	178.1	179.0	186.5 140	151.6	141.6	54.34	80.64 126	113.1	25 RT	66b1, 58B2 51B1
ceramics	166 150 165.6	168 150	162 146	189 171 180.7	76.6 66	78.2 68	77.5 66	71.0 57	42.9 44	54.6 57	44.8 43	25 25	56B3 64b1 55H5
									42.48	53.02	45.65	25	

Tab. 42 ... 45 see page 58

Tab. 46. BaTiO₃. Summary of the ESR parameters for various paramagnetic centers in doped BaTiO₃.

Para-magnetic center	Site	S	g	ν GHz	T °K	g-factor	FS		HFS		Ref.	Literature
							$D, E, a, F [10^{-3} \text{ m}^{-1}]$		I	$A, B [10^{-3} \text{ m}^{-1}]$		
Mn ²⁺	Ti ⁴⁺	5/2	(7)	9.3	78	2.0016 ± 0.0005	$D = 56 \pm 5$		5/2	$^{55}\text{A}_{ } = ^{55}\text{A}_{\perp} = 79.8 \pm 0.5$	a)	60I1
					300	2.0023 ± 0.0005	$D = 65 \pm 5$			$^{55}\text{A}_{ } = 78.6 \pm 0.5$	b)	63O1
					440	2.0009 ± 0.001	$a = 14 \pm 5$			$^{55}\text{A}_{ } = 79 \pm 0.5$	c)	64I5
	Ba ²⁺	5/2	(7)	9.3	RT	2.002 ± 0.001	$D = +(215 \pm 2)$ $a = +(16.76 \pm 0.94)$			$^{55}\text{A}_{ } = -(77.4 \pm 0.6)$ $^{55}\text{A}_{\perp} = -(82.3 \pm 0.8)$		
					438	2.002 ± 0.001	$D = 0$ $a = +(12.11 \pm 0.94)$			$^{55}\text{A}_{ } = ^{55}\text{A}_{\perp} = -(79.3 \pm 0.4)$		66I3 ¹⁾

Para-magnetic center	Site	S	g	ν GHz	T °K	g-factor	FS		HFS		Ref.	Literature
							$D, E, a, F, b [10^{-3} \text{ m}^{-1}]$		I	$A, B [10^{-3} \text{ m}^{-1}]$		

D_{33}^{exp}	χ^2/ν	χ^2	ν	$D = 0$ $a = +(12.11 \pm 0.94)$	$E = 0$	${}^{55}A_{ } = {}^{55}A_{\perp}$ ${}^{55}A_{ } = -(79.3 \pm 0.4)$	$0.01 \text{ } ^{\circ} / ^{\circ}$
438		2.002 \pm 0.001					

Para-magnetic center	Site	S	J	ν GHz	T °K	g-factor	FS		HFS		Ref.	Literature
							D, E, a, F, b [10^{-3} m^{-1}]	I	A, B [10^{-3} m^{-1}]			
Fe ³⁺	Ti ⁴⁺	5/2	(7)	5 ... 7.5, 10, 16.3 10	393, 433	2.003	$D = 0$ $a = 102 \pm 12$				d)	59H5, 62R1
					300	2.0036 ± 0.002	$D = +929$ $a = +91 \pm 20$	$E = 0$		e)	63S2 ^{a)}	
					276	2.0036 ± 0.002	$D = -530 \pm 10$ $a = +105 \pm 20$			f)		
					213	2.0036 ± 0.002	$D = -640 \pm 10$ $E = 0 \pm 1.3$					
					77	2.0036 ± 0.002	$D = 0$ $a = +115 \pm 10$	$E = 0$				
Co ²⁺	Ti ⁴⁺	1/2	(3)	9	173	2.003 ± 0.002	$D = -23 \pm 5$ $a - F = +113 \pm 10$				64S3 ^{a)}	
					4	4.347 (isotropic)			7/2	$^{59}A_{ } = ^{59}A_{\perp}$ $^{59}A_{ } = 109$		67Z2
Gd ³⁺	Ba ²⁺	7/2	(8)	12, 18 10	300	1.995 ± 0.003	b_{80}	b_{40}	b_{60}			62R1
					425	1.995 ± 0.003	—	≈ 6	1.6 ± 1.0			
					RT	1.992	—	24 ± 0.9	-3.7 ± 2.8			64T1
					436	1.992	—	23.3 ± 0.4	-1.8 ± 0.4			66T3
						$g_{ }$	g_{\perp}					
Pt ³⁺	Ti ⁴⁺	1/2	(3)	10	4	1.950 ± 0.005	2.459 ± 0.003				66S21	
					78	1.935 ± 0.005	2.51 ± 0.02					63S12
Electron	oxygen vacancy	1/2	(2)	10	55	1.930	1.911			g)	63S11, 66T2, 67T3	

^a Temperature dependence of D^s in the tetragonal phase is linear. $[65V4]$.

a) Temperature dependence of D^s in the tetragonal phase is linear. [65V4].

b) Forbidden transition lines ($\Delta M = \pm 1, \Delta m = \pm 1$) are observed. [63O1], [64I5]. Forbidden transition lines ($\Delta M = \pm 1, \Delta m = \pm 1$) are observed. [65I1], [66I3].

b) Forbidden transition lines ($\Delta M = \pm 1, \Delta m = \pm 1, \Delta l = 0$) are observed. [67Zr], [67Zr], [67Zr].

g) Temperature dependence of ^{88}A . [$6\frac{1}{2}\text{T}$].

(1) Fe^{3+} spectra are studied with a d.c. bias electric field near transition temperature from cubic to rhombohedral phase. [64S].

e) Forbidden transition lines ($\Delta M = 2, 3, 4, 5$) are observed in the rhombohedral phase. [65c].

(f) Fe^{3+} spectra due to the oxygen vacancy; $g_{\parallel} \approx 2$, $g_{\perp} = 6.0 \pm 0.1$ at 77°K [64d].

g) Hyperfine structure of an electron captured by an oxygen vacancy. [64D1].

- 1) Mn^{3+} ion takes the place of Fe^{3+} ion.

- 2) Positive α is assumed.

Tab. 42. BaTiO₃, SrTiO₃, TiO₂, KTaO₃. Dispersion parameters calculated from the Kramers-Kronig analysis [62S11]. See Fig. 201

$$\kappa' = \kappa_{\infty} + \sum_i 4\pi\epsilon_i \nu_i^2 \frac{\nu_i^2 - \nu^2}{(\nu_i^2 - \nu^2)^2 + \gamma_i^2 \nu^2} \quad \kappa'' = \sum_i 4\pi\epsilon_i \nu_i^2 \frac{\gamma_i \nu}{(\nu_i^2 - \nu^2)^2 + \gamma_i^2 \nu^2}$$

	BaTiO ₃ Ordinary ray	SrTiO ₃	TiO ₂ Ordinary ray	KTaO ₃
$\lambda_1; \nu_1$	20.4; 491	18.4; 544	20.0; 500	18.2 ± 0.2; 549 ± 6
γ_1/ν_1	0.059 ± 0.002	0.049 ± 0.002	0.044 ± 0.004	0.043 ± 0.009
$4\pi\epsilon_1$	0.60 ± 0.03	1.56 ± 0.06	2.0 ± 0.2	2.4 ± 0.5
$\lambda_2; \nu_2$	54.8; 183	56.3 ± 0.5; 178 ± 2.0	25.8; 388	49.8; 200.8
γ_2/ν_2	0.030 ± 0.006	0.039 ± 0.004	0.058 ± 0.006	0.055 ± 0.011
$4\pi\epsilon_2$	2.2 ± 0.4	3.6 ± 0.4	1.08 ± 0.1	7.6 ± 1.5
$\lambda_3; \nu_3$	296 ± 8; 33.8 ± 0.9	114.3 ± 1.1; 87.7 ± 0.9	54.8 ± 0.5; 183 ± 1.8	107.5 ± 2.0; 93.0 ± 2.0
γ_3/ν_3	2.5 ± 0.1	0.5 ± 0.1	0.19 ± 0.01	0.5 ± 0.1
$4\pi\epsilon_3$	1830 ± 70	311 ± 62	81.5 ± 4.1	163 ± 33

Resonance wavelength λ_i in 10⁻⁸ m; resonance frequency ν_i in 10² m⁻¹; width γ_i ; strength $4\pi\epsilon_i$.Tab. 43. BaTiO₃, SrTiO₃, TiO₂. Energies of fundamental absorption edges (in eV) at RT. [65C2]

	E_0	A_1	A_2	A_3	B_1	B_2	C_1	C_2	D	E	
SrTiO ₃	3.2	4.00	4.86	5.5	6.52	7.4	9.2	9.9	12.5	15.3	eV
BaTiO ₃	3.2	3.91	4.85		6.10	7.25	10.3	11.8	12.8	15	eV
TiO ₂ (E ⊥ c)		3.97	5.52		6.50	7.64	8.53	9.24	11	14.1	eV

Tab. 44. BaTiO₃, SrTiO₃, KTaO₃, KTa_{0.35}Nb_{0.65}O₃ (KTN), TiO₂. Band gap energies $\hbar\omega_g$ (in eV). [67B1]. See Fig. 46, 103, 216, 430. F_1, F_2 : different dispersion functions $F_i(\omega/\omega_g)$, see [67B1]

	SrTiO ₃		BaTiO ₃	KTaO ₃		KTN	TiO ₂	
	296 °K	77 °K	403 °K	296 °K	77 °K	296 °K	296 °K	
Faraday rotation $\hbar\omega_g$ for F_1	3.40	3.43	3.25	3.77	3.79	3.54	3.62	eV
Faraday rotation $\hbar\omega_g$ for F_2	3.21	3.26	3.11	3.62	3.65	3.36	3.37	eV
Energy of reflectivity peak or shoulder	3.20	—	3.20	—	—	3.70	—	eV
Energy of electroreflectance singularity	—	—	3.20	3.57	—	3.60	3.00	eV
$\hbar\omega_g$ from absorption data	3.40	—	—	3.80	—	—	3.30	eV
Energy at which absorption coefficient $\alpha \approx 10^4$ cm ⁻¹	3.37	—	3.26	3.79	—	3.45	3.18	eV

Tab. 45. BaTiO₃ (reduced or doped). List of reference papers on PTC anomaly

Materials (dopants)	References	Materials (dopants)	References
Single crystal BaTiO ₃ : reduced	57H1, 63K3, 64I4, 64G4, 65M1, 65U2 64B11	Ceramics BaTiO ₃ BaTiO ₃ : La	63H5, 65U2 59S1, 63T3, 64J1, 65M1 63T3
BaTiO ₃ : Nb		BaTiO ₃ : Ce BaTiO ₃ : Sm BaTiO ₃ : Gd BaTiO ₃ : Sb (Ba-Sr)TiO ₃ (Ba-Sr)TiO ₃ : La BaTiO ₃ : Sr, Ce, Sn BaTiO ₃ : Sr, Ca, Sn BaTiO ₃ : Sr, Bi BaTiO ₃ : Mg, Ce BaTiO ₃ : Zr, Ce BaTiO ₃ : Si, Ce	63G5 65U2 65A3 61H5, 65A3 59S1, 61T1, 63T3 61S1 61S1 63T3 61S1 61S1 61S1

Nr. 1A-

1a F

b pl

st

cr

sp

Θ

a

2a C

b C

3 C

P

4 T

I

5a D

au

C

6a S

A

A

c T

7a F

9a E

I

F

12b E

14a I

16 F

T

P:

—

—

* Phase

Nr. 1A-9 PbTiO₃, Lead titanate

1a	Ferroelectric activity was reported independently by SHIRANE et al. and by SMOLENSKII in 1950.			50S4 50S6
b	phase	III ^b *)	II ^a)	I ^a)
	state		F ^a)	P ^a)
	crystal system		tetragonal ^c)	cubic ^a)
	space group		P4mm-C _{4v} ¹	Pm3m-O _h ¹
	Θ	-100 ^b)	490 ^a)	°C
	$a = 3.904_4 \text{ Å}, c = 4.152_4 \text{ Å}$ at RT (in phase II).			46M2
2a	Crystal growth: KF flux method; PbCl ₂ flux method.			58K1, 52N2
b	Crystal form: Fig. 271.			
3	Crystal structure: Positional parameters: Tab. 47, 48. Projection of crystal structure: Fig. 272, 273.			
4	Thermal expansion: Fig. 274 ... 280. Dependence of lattice parameters on hydrostatic pressure: Fig. 281.			
5a	Dielectric constants: Fig. 282. Small dielectric anomaly was observed at about -100 and -150 °C. Curie-Weiss constant: $C = 1.1 \cdot 10^5 \text{ °K}$ (single crystal).			56K2 62B4
6a	Specific heat: Fig. 283.			
		II-I		
	ΔQ_m	1150	cal mol ⁻¹	51S7
c	ΔS_m	1.6	cal °K ⁻¹ mol ⁻¹	51S7
	Thermal conductivity: Fig. 284.			
7a	Piezoelectric properties: Tab. 49.			
9a	Birefringence: Fig. 285. Infrared absorption: Fig. 286, 287. Frequencies of infrared modes: Tab. 50.			
12b	ESR: Tab. 51.			
14a	Domain structures were observed by polarized light.			52N2, 58K1, 59K1
16	Radiation damage: Fig. 288.			

Tab. 47. PbTiO₃. Positional parameters of atoms at RT. [56S5]

	<i>x</i>	<i>y</i>	<i>z</i>
Pb	0	0	0
Ti	$\frac{1}{2}$	$\frac{1}{2}$	0.540
O(1)	$\frac{1}{2}$	$\frac{1}{2}$	0.112
O(2)	$\frac{1}{2}$	0	0.612
	0	$\frac{1}{2}$	0.612

Tab. 48. PbTiO₃. Bond lengths in Å at RT (phase II) and at 490 °C (phase I) [56S5]. O(1)₊ represents the O(1) ion closer to, O(1)₋ that further away from Ti. Similarly O(2)₊ is closer to Pb

phase	II (at RT)	I (at 490 °C)
Ti-O(1) ₊	1.78	1.89
Ti-O(1) ₋	2.38	
Ti-O(2)	1.98	
Pb-O(1)	2.80	2.80
Pb-O(2) ₊	2.53	
Pb-O(2) ₋	3.20	

Phase transition II-III was reported to occur only if the cooling rate is extremely slow. [55K3]

Tab. 49. PbTiO_3 (modified ceramics). Electromechanical constants at RT. [68U1]

Additive	$\text{PbNb}_{4/5}\text{O}_3$ 5.0 mol%	$\text{BiZn}_{1/2}\text{Ti}_{1/2}\text{O}_3$ 5.0 mol%	$\text{Bi}_{2/3}\text{Zn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ 5.0 mol%	
a	3.915	3.904	3.911	Å
c	4.104	4.148	4.133	Å
c/a	1.049	1.062	1.057	
ρ	7.19	7.68	7.12	10^3 kg m^{-3}
porosity	0.105	0.036	0.10	
Θ	466	524	494	$^\circ\text{C}$
κ_{11}^T	—	195	244	
κ_{33}^T	226	147	203	
d_{31}	10	3.9	7.4	$10^{-12} \text{ C N}^{-1}$
d_{33}	37	37	47	$10^{-12} \text{ C N}^{-1}$
g_{31}	5.2	3.0	4.1	$10^{-8} \text{ m}^2 \text{ C}^{-1}$
g_{33}	16	28	28	$10^{-8} \text{ m}^2 \text{ C}^{-1}$
s_{11}^E	1.2	1.2	1.1	$10^{-11} \text{ m}^2 \text{ N}^{-1}$
s_{33}^E	1.1	0.95	1.1	$10^{-11} \text{ m}^2 \text{ N}^{-1}$
Q_{mech} for s_{11}	—	—	—	
for s_{33}	336	54	326	
k_{15}	—	0.40	0.36	
k_{31}	0.068	0.031	0.052	
k_{33}	0.23	0.32	0.35	

Tab. 50. PbTiO_3 . Wave numbers in 10^3 m^{-1} and symmetries of infrared modes of lattice vibration obtained from Kramers-Kronig analysis of the reflectance data at RT. [65P4]

$\tilde{\nu}_1$ (Ti-O stretch)	$\tilde{\nu}_2$ (Ti-O ₃ torsion)	$\tilde{\nu}_3$ (O-Ti-O bend)	$\tilde{\nu}_4$ (cation-TiO ₃ lattice mode)
530 (E_u, A_1)	400 (B_1, E_u)	220 (E_u, A_1) 172	83 (E_u, A_1)

Tab. 51. PbTiO_3 . g -factors at RT. [64G1]

Paramagnetic center	Site	S	\mathcal{H}	ν GHz	T $^\circ\text{K}$	g -factor	
						g_{\parallel}	g_{\perp}
Fe^{3+}	Ti^{4+}	1/2*	(2)	8.8	RT	2.009 ± 0.005	5.97 ± 0.02

The spectrum up to 300 $^\circ\text{C}$ and down to -120 $^\circ\text{C}$ did not show any fundamental change.

Nr. 1A-10 CaZrO_3 , Calcium zirconate

1	A few physical properties of CaZrO_3 were studied in comparison with those of some perovskite-type ferroelectrics. The crystal was reported to be orthorhombic with the cell dimensions $a = 5.587$ Å, $b = 8.008$ Å, $c = 5.758$ Å at RT.	
4	Linear thermal expansion: $\alpha = 8.55 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$ between 23 $^\circ\text{C}$ and 223 $^\circ\text{C}$; $\alpha = 9.53 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$ between 223 $^\circ\text{C}$ and 333 $^\circ\text{C}$ for ceramics of bulk density $\rho = 4.95 \cdot 10^3 \text{ kg m}^{-3}$	55C1 65B10
9	Infrared absorption: Fig. 289, 290; Tab. 52.	

Tab. 52. CaZrO_3 . Wave numbers in 10^3 m^{-1} and symmetry of infrared modes of lattice vibration obtained from Kramers-Kronig analysis of the reflectance data at RT. [65P4]

$\tilde{\nu}_1$ (Zr-O stretch)	$\tilde{\nu}_2$ (Zr-O ₃ torsion)	$\tilde{\nu}_3$ (O-Zr-O bend)	$\tilde{\nu}_4$ (cation-ZrO ₃ lattice mode)
515 (B_1, B_2, A_1)	340 (B_1, B_2, A_1) (377) (418)	228 (B_1, B_2, A_1) 186	153 (B_1, B_2, A_1) 96

* The fictitious spin is $\frac{1}{2}$ [64G1].

Nr. 1A-11 SrZrO₃, Strontium zirconate

1	A few physical properties of SrZrO ₃ were studied in comparison with those of some perovskite-type ferroelectrics. The crystal was reported to be pseudo-cubic with $a' = 4.099 \text{ \AA}$ at RT.	57R2
4	Linear thermal expansion: $\alpha = 8.75 \cdot 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ between 23 °C and 320 °C; $\alpha = 9.34 \cdot 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ between 320 °C and 700 °C for ceramics of bulk density $\rho = 5.00 \cdot 10^3 \text{ kg m}^{-3}$.	65B10
9	Infrared absorption: Fig. 291, 292; Tab. 53.	

Tab. 53. SrZrO₃. Wave numbers in 10^3 m^{-1} and symmetry of infrared modes of lattice vibration obtained from Kramers-Kronig analysis of the reflectance data at RT. [65P4]

$\tilde{\nu}_1$ (Zr-O stretch)	$\tilde{\nu}_2$ (Zr-O ₃ torsion)	$\tilde{\nu}_3$ (O-Zr-O bend)	$\tilde{\nu}_4$ (cation-ZrO ₃ lattice mode)
522 (B_1, B_2, A_1)	325 (B_1, B_2, A_2) (357) (379)	240 (B_1, B_2, A_1)	143 (B_1, B_2, A_1)

Nr. 1A-12 BaZrO₃, Barium zirconate

1	A few properties of BaZrO ₃ were reported in comparison with those of some perovskite-type ferroelectrics. The crystal was reported to be cubic with the cell dimensions $a = 4.192 \text{ \AA}$ at RT.	57R2
4	Linear thermal expansion: $\alpha = 5.64 \cdot 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ between 23 °C and 214 °C; $\alpha = 6.54 \cdot 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ between 214 °C and 324 °C for ceramics of bulk density $\rho = 6.73 \cdot 10^3 \text{ kg m}^{-3}$.	65B10
9	Infrared absorption: Fig. 293, 294; Tab. 54.	

Tab. 54. BaZrO₃. Wave numbers in 10^3 m^{-1} and symmetries of infrared modes of lattice vibration obtained from Kramers-Kronig analysis of the reflectance data at RT. [65P4]

$\tilde{\nu}_1$ (Zr-O stretch)	$\tilde{\nu}_2$ (Zr-O ₃ torsion)	$\tilde{\nu}_3$ (O-Zr-O bend)	$\tilde{\nu}_4$ (cation-ZrO ₃ lattice mode)
505 (F_{1u})	— (F_{2u})	210 (F_{1u})	115 (F_{1u})

Nr. 1A-13 PbZrO₃, Lead zirconate

1a	Dielectric anomaly of PbZrO ₃ associated with a phase transition was reported independently by ROBERT and by SMOLENSKII in 1950. Antiparallel ionic shifts on the (001) projection of crystal structure were found by SAWAGUCHI et al. in 1951. In the same year antiferroelectric double hysteresis loops were discovered by SHIRANE et al.. PbZrO ₃ is the first compound in which double hysteresis loops were observed.		50R1, 50S7 51S3 51S8
b.	phase	II ^a)	I ^a)
	state	A ^b)	P ^a)
	crystal system	orthorhombic ^c)	cubic ^c)
	space group	Pba2-C _{2v} ^c)	Pm3m-O _h ^c)
	230 °C ^a)		
	θ $a = 5.87 \text{ \AA}$, $b = 11.74 \text{ \AA}$, $c = 8.20 \text{ \AA}$ at RT (in phase II). The cubic unit cell in phase I becomes pseudo-tetragonal in phase II. The pseudo-tetragonal cell constants a' and c' are related with the orthorhombic cell constants a , b and c : $a = \sqrt{2} a'$, $b = 2\sqrt{2} a'$ and $c = 2c'$, where $a' = 4.15 \text{ \AA}$, $c' = 4.10 \text{ \AA}$ at RT. Relation between the pseudo-tetragonal and orthorhombic cells: Fig. 295.		51S3
2a	Crystal growth: PbCl ₂ flux method.		55J2

3	Nr. 1A-13 PbZrO ₃ , continued Z = 8 (in phase II). The crystal is polar along the <i>c</i> axis and antipolar along the <i>a</i> axis in phase II. Fig. 295 shows schematically the shifts of Pb ions. Positional parameters and shifts from ideal perovskite positions: Tab. 55. Projection of ZrO ₆ : Fig. 296, 297, 298. Bond distances between Zr and O: Fig. 299.	51S3, 57J4, 51S3 57J4
4	Thermal expansion: Fig. 300 ... 303. $\alpha_{a'} \cong -0.05 \cdot 10^{-5} \text{ }^{\circ}\text{K}^{-1}$ and $\alpha_{c'} \cong 2.80 \cdot 10^{-5} \text{ }^{\circ}\text{K}^{-1}$ in phase II; $\alpha_{a'} \cong 1.10 \cdot 10^{-5} \text{ }^{\circ}\text{K}^{-1}$ in phase I, where $\alpha_{a'}$ and $\alpha_{c'}$ are the linear thermal expansion coefficients along the pseudo-tetragonal <i>a'</i> and <i>c'</i> axes, respectively.	52S1
5a	Dielectric constants: Fig. 304. $C = 1.36 \cdot 10^5 \text{ }^{\circ}\text{K}$ (determined with ceramics). Effect of pressure: Fig. 305. $(d\epsilon_a/dp)_{p \rightarrow 0} = (4.1 \pm 0.2) 10^{-8} \text{ }^{\circ}\text{K N}^{-1} \text{ m}^2$.	50R1
c	Critical field: Fig. 306.	66R2
6a	Specific heat: Fig. 307. For the transition II-I: $\Delta Q_m = 440 \text{ cal mol}^{-1}$; $\Delta S_m = 0.88 \text{ cal }^{\circ}\text{K}^{-1} \text{ mol}^{-1}$.	52S2
b	Thermal conductivity: Fig. 308.	
8	Elastic compliances: Fig. 309.	
9a	Birefringence: Fig. 310. Infrared absorption: Fig. 311, 312; Tab. 56.	
16	Radiation damage: Fig. 313.	

Tab. 55. PbZrO₃ (ceramics). Atomic coordinates and shifts from ideal perovskite positions at RT. [57J4]

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Wyckoff notation	Total shift Å
Pb'	0.706	0.127	0	4 <i>c</i>	0.26
Pb''	0.706	0.127	0.500	4 <i>c</i>	0.26
Zr'	0.243	0.124	0.250	4 <i>c</i>	0.04
Zr''	0.243	0.124	0.250	4 <i>c</i>	0.04
O(1)'	0.270	0.150	0.980	4 <i>c</i>	0.35
O(1)''	0.270	0.100	0.480	4 <i>c</i>	0.35
O(2)'	0.040	0.270	0.300	4 <i>c</i>	0.53
O(2)''	0.040	0.270	0.750	4 <i>c</i>	0.34
O(3)'	0	0.500	0.250	2 <i>b</i>	0
O(3)''	0	0.500	0.800	2 <i>b</i>	0.41
O(4)'	0	0	0.250	2 <i>a</i>	0
O(4)''	0	0	0.800	2 <i>a</i>	0.41

Tab. 56. PbZrO₃. Wave numbers in 10² m⁻¹ and symmetries of infrared modes of lattice vibration obtained from Kramers-Kronig analysis of the reflectance data at RT. [65P4]

$\tilde{\nu}_1$ (Zr-O stretch)	$\tilde{\nu}_2$ (Zr-O ₃ torsion)	$\tilde{\nu}_3$ (O-Zr-O bend)	$\tilde{\nu}_4$ (cation-ZrO ₃ lattice mode)
508 (<i>E_u</i> , <i>A₁</i>)	290 (<i>B₁</i> , <i>E_u</i>)	221 (<i>E_u</i> , <i>A₁</i>)	80 (<i>E_u</i> , <i>A₁</i>) 34

Nr. 1A-14 PbHfO₃, Lead hafnate

1a	A dielectric anomaly associated with a phase transition was observed, and the possibility of the antiferroelectricity was discussed by SHIRANE et al. in 1953.				53S3
b	phase	III	II	I	53S3
	state	(A)		P	
	crystal system	pseudo-tetragonal	tetragonal	cubic	
	θ	163	215	$^{\circ}\text{C}$	
Lattice constants for the pseudo-tetragonal phase: $a' = 4.136 \text{ \AA}$, $c'/a' = 0.991$ at RT.					53S3

4

Thermal expansion: Fig. 314.
Cubic thermal expansion coefficients: below 158 °C: $20 \cdot 10^{-6} \text{ deg}^{-1}$;
above 215 °C: $27 \cdot 10^{-6} \text{ deg}^{-1}$.

53S3

5a

Dielectric constant: Fig. 315.
 $C = 9.5 \cdot 10^4 \text{ °K (ceramics)}$.

53S3

Nr. 1A-15 BiFeO₃, Bismuth ferrite

1a

In 1960*) it was pointed out on the basis of x-ray studies of the solid solution, PbTiO₃-BiFeO₃, that BiFeO₃ could have a ferroelectric Curie point at high temperatures. The Curie point was estimated to be about 850 °C from studies of the same solid solution^{b)}. Disagreement, however, exists among many experimental data reported so far, therefore reservation is necessary in deciding whether BiFeO₃ is ferroelectric or antiferroelectric. Antiferromagnetic anomaly in BiFeO₃ was observed by direct magnetic measurements at about 370 °C^{c)}.

b

phase	IV	III	II	I
state	(A) or (F), A_{magn}^*	(A) or (F), P_{magn}	(A) or (F), P_{magn}	(P), P_{magn}
crystal system	rhombohedral	rhombohedral	rhombohedral	cubic (possibly)
space group	R3m-C _{3v} ^{**}			
θ	370	≈ 575	850	°C

$a = (3.962 \pm 0.001) \text{ Å}$, $\alpha = 89^\circ 31' \pm 3'$ at RT.
Further references are available on unit cell parameters.

3

Crystal structure: From the x-ray diffraction studies, BiFeO₃ was found to belong to one of the five space groups: R 3, $R \bar{3}$, R 32, R3m and $R\bar{3}m$. Neutron diffraction studies suggested that BiFeO₃ belongs to the non-centrosymmetric space group R3m. The crystal structure can be regarded as consisting of alternating FeO₆ and BiO₆ trigonal pyramids: Fig. 316; Tab. 57. According to the electron diffraction study, BiFeO₃ belongs to the non-centrosymmetric space group R3m at RT. Atomic coordinates: Tab. 58. The space group R3m was, however, rejected by SMOLENSKII et al., because it does not satisfy the conditions for the existence of weak ferromagnetism. The magnetic structure of BiFeO₃ was proved to be G-type by the neutron diffraction experiments. Fig. 317, 318.

4

Unit cell parameters: Fig. 319, 320. See also

66R8, 64T5

5a

Dielectric constant: Fig. 321, 322, 323.
No reliable data on the dielectric constant in the high temperature region near 850 °C are available.

11

Magnetic susceptibility: Fig. 324.
At RT, no spontaneous magnetic moment was observed in the fields up to 22 kOe.

12c

Mössbauer effect: Fig. 325, 326.

17

Calculations of the internal electric fields and their gradients in BiFeO₃ crystals were made on the basis of an ionic model.

67T7

Tab. 57. BiFeO₃. Values of the interatomic distances [Å]. [63K5]. See Fig. 316. See also [64T6]

	520 °C	20 °C
Bi-Fe (A)	3.841	3.857
Bi-Fe (B)	3.006	2.994
Bi-O (C)	2.903	2.907
Bi-O (D)	2.680	2.693
Fe-O (F)	2.233	2.214
Fe-O (G)	1.754	1.774
O-O (H)	2.841	2.859
O-O (K)	2.800	2.800
O-O (L)	2.680	2.724

Tab. 58. BiFeO₃. Atomic coordinates. [64T6]

Atom	x	y	z
Bi	0.0337	0.0337	0.0337
Fe	0.5000	0.5000	0.5000
O(1)	-0.0280	0.5000	0.5000
O(2)	0.5000	-0.0280	0.5000
O(3)	0.5000	0.5000	-0.0280

* This state is presumably weak ferromagnetic. [66Y2]

** See subsection 3.

Nr. 1A-16 KIO_3 , Potassium iodate

1a	Ferroelectric behavior in KIO_3 was reported by HERLACH in 1961.					61H3
b	phase	V ^{a)}	IV ^{a)}	III ^{a)}	II ^{a)}	a)61H3
	state		F ^{a)}	F ^{a)}	F ^{a)}	
	crystal system			trigonal ^{b)} *		b)60S5
	Θ	-190 ^{a)}	-18, -10 ^{a)} **	70 ^{a)}	212 ^{a)}	°C
	$T_{\text{melt}} = 560^\circ\text{C}$. $\rho = 3.979^{1)} \cdot 10^3 \text{ kg m}^{-3}$. ¹⁾ A different value, 3.802, is also given in the same reference. $a = (4.410 \pm 0.005) \text{ \AA}$, $\alpha = 89.41^\circ$ at RT, adopting trigonal system. $a = 8.921 \text{ \AA}$, $b = 8.916 \text{ \AA}$, $c = 8.885 \text{ \AA}$, $\alpha \cong \beta \cong \gamma \cong 90^\circ \pm 30'$ at RT, adopting triclinic system. Transparent					66H17 08g1 60S5 65F3
2a	Hydrothermal method: Fig. 327. Growth from the supersaturated solution with 10 ... 14% HIO_3 at a constant temperature: Fig. 328.					61H3 27m1
3	$Z = 1$ in phase III, adopting trigonal system. $Z = 8$ in phase III, adopting triclinic system.					61H3 65F3
4	Lattice deformation: $a = [4.44 + 0.00022 (T - 220)] \text{ \AA}$, $\alpha = 89^\circ 20' - 0.09 (T - 220)'$ in phase I (T in $^\circ\text{C}$).					61H3
5a	Dielectric constants: Fig. 329, 330.					66H17
c	Spontaneous polarization: Fig. 331.					61H3
9a	Absorption edge: Fig. 332.					67V2
12a	NMR: Fig. 333.					61H3

1B Complex perovskite-type oxides

Nr. 1B1-i $(\text{K}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$, Potassium bismuth titanate

1a	Ferroelectricity in $(\text{K}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ was found by SMOLENSKII and AGRANOVSKAYA in 1959.				59S6
b	phase	III	II	I	
	state	(F)	(A)	P	
	crystal system	tetragonal	pseudo-cubic	cubic	62I5
	space group			$\text{Pm}\bar{3}\text{m}-\text{O}_h^1$	a)60S6
	Θ	270	410,380 ^{a)}	°C	
	$a = (3.913 \pm 0.003) \text{ \AA}$, $c = (3.993 \pm 0.003) \text{ \AA}$ at RT.				
3	Crystal structure: Disordered perovskite.				62I5
4	Lattice distortion: Fig. 334. Thermal expansion: Fig. 335.				
5a	Dielectric constant: Fig. 336.				

Nr. 1B1-ii $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$, Sodium bismuth titanate

1a	Ferroelectricity in $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ was found by SMOLENSKII and AGRANOVSKAYA in 1959.	59S6
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* Various crystal systems have been proposed: trigonal [60S5], triclinic [65F3].
 ** -10°C on heating, -18°C on cooling.

* Various crystal systems have been proposed: trigonal [60S5], triclinic [65F3].
 ** -10 $^\circ\text{C}$ on heating, -18 $^\circ\text{C}$ on cooling.

1b	phase	III	II	I	62I5
	state	F	(A)	P	
	crystal system	rhombohedral	pseudo-cubic	cubic	
	space group			Pm3m-O _h ¹	
	Θ	≈200 ^a) 320 °C			
a = (3.891 ± 0.002) Å, α = 89° 36' ± 3' at RT.					
3	Crystal structure: Disordered perovskite.				62I5
4	Thermal expansion: Fig. 337.				
5a	Dielectric constant: Fig. 338.				60S6
c	Spontaneous polarization and coercive field: P _s ≈ 8.0 · 10 ⁻² C m ⁻² ; E _c ≈ 14 · 10 ² kV m ⁻¹ at 116 °C.				

Nr. 1B2-i $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$

1a	Antiferroelectric properties of $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ were discovered by SMOLENSKII et al. in 1959.			59S7
b	phase	II	I	62Z1
	state	A	P	
	crystal system	orthorhombic	cubic	
	space group	$\text{C}222_1\text{-D}_2^5$		
	Θ	38 °C		
	$a = 22.74 \text{ \AA}$, $b = 22.79 \text{ \AA}$, $c = 15.90 \text{ \AA}$ at RT. Orthorhombic unit cell: see Fig. 339.			
2a	Crystal growth: Crystal growth of $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ was reported by MYL'NIKOVA.			60M2
3	Crystal structure: $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ has the structure of perovskite type. Fig. 339. $Z = 64$ (molecular unit: Pb_2MgWO_6).			62Z1
4	Lattice distortion associated with the phase transition. Thermal expansion: Fig. 340.			62Z1
5a	Dielectric constants: Fig. 341, 342, 343. $d\epsilon_a/dp = -5.84 \cdot 10^3 \text{ }^\circ\text{K N}^{-1}\text{m}^2$.			
6	Specific heat: Fig. 344. Transition heat (II \rightarrow I): $\Delta Q_m = 276 \text{ cal mol}^{-1}$.			66S28
8a	Elastic compliance: Fig. 345. Ultrasound absorption: Fig. 346, 347.			

Nr. 1B2-ii $\text{Pb}(\text{Cd}_{1/2}\text{W}_{1/2})\text{O}_3$

1a	Synthesis of $\text{Pb}(\text{Cd}_{1/2}\text{W}_{1/2})\text{O}_3$ was reported by BELYAEV et al. in 1963.			63B3
b	phase	II	I	65F4
	state	(A)	P	
	crystal system	monoclinic	cubic	
	Θ	400 °C		
	$a = (4.156 \pm 0.002) \text{ \AA}$, $b = (4.074 \pm 0.002) \text{ \AA}$, $\beta = 91^\circ 9' \pm 5'$ at RT. ROGINSKAYA and VENEVTSEV reported that another transition exists at 120 °C, in addition to the transition at 400 °C.			
3	Crystal structure: Superstructure lines, indicating ordered location of the octahedral voids of the perovskite lattice, were observed.			65R4
4	Lattice distortion: Fig. 348, 349.			65F4
5a	Dielectric constant: Fig. 350.			

1.1 Oxide des Perowskit-Typs

Nr. 1B2-iii $\text{Pb}(\text{Mn}_{1/2}\text{W}_{1/2})\text{O}_3$

1a	A synthesis of $\text{Pb}(\text{Mn}_{1/2}\text{W}_{1/2})\text{O}_3$ was reported by VENEVTSEV et al.			64V3
b	phase	II	I	
	state	(A), P_{magn}	P, P_{magn}	
	crystal system	monoclinic	cubic	
	Θ	423	°K	65R5
	$a = 4.063 \text{ \AA}$, $b = 4.033 \text{ \AA}$, $\beta = 90^\circ 12'$ at RT.			
5a	Dielectric constant: Fig. 351.			65R5
10	Electrical conductivity: $\sigma = 8 \cdot 10^{-8} \Omega^{-1} \text{ m}^{-1}$.			65R5
11	Magnetic susceptibility: see Fig. 351.			

Nr. 1B2-iv $\text{Pb}(\text{Co}_{1/2}\text{W}_{1/2})\text{O}_3$

1a	Antiferro- and ferroelectric properties in $\text{Pb}(\text{Co}_{1/2}\text{W}_{1/2})\text{O}_3$ were discovered by FILIP'EV et al.					63F1
b	phase	IV	III	II	I	65B8
	state	F, F_{magn} (weak)	F, P_{magn}	A, P_{magn}	P, P_{magn}	a) 66K6 b) 64F4
	crystal system			orthorhombic	cubic	
	Θ	9a)	83 ... 103	293b)	305	°K
	$a = 4.008 \text{ \AA}$ at 298 °K.					
2a	Crystal growth: Flux method with PbO.					65B8
3	Crystal structure: A superstructure was observed which was completely explained by alternation of the population of the oxygen octahedra by Co^{2+} and W^{6+} cations along the three directions. The real elementary lattice is a cubic face centered one with the parameter $A = 2a$ for phase I and with the parameters $A = 2 \cos(\beta/2)$, $B = 2b$, and $C = 2a \sin(\beta/2)$ for II, where a , b and β are the parameters of the perovskite sub-lattice.					64F4
4	phase	lattice parameters				
	I	$A = 8.017 \text{ \AA}$ at 298 °K				
	II	$A = 5.669 \text{ \AA}$, $B = 7.956 \text{ \AA}$, $C = 5.689 \text{ \AA}$ at 258 °K				
	Lattice distortion: Fig. 352.					64F4
5a	Dielectric constant: Fig. 353, 354, 355.					
c	Polarization: Fig. 356.					
11	Magnetic susceptibility and magnetization: Fig. 357, 358.					

Nr. 1B2-v $\text{Pb}(\text{Mn}_{1/2}\text{Re}_{1/2})\text{O}_3$

1a	A synthesis of $\text{Pb}(\text{Mn}_{1/2}\text{Re}_{1/2})\text{O}_3$ was reported by VENEVTSEV et al.			64V3	
b	phase	III	II	I	
	state	(A), F_{magn}	(A), P_{magn}	P, P_{magn}	
	crystal system		monoclinic	cubic	
	Θ	103	393	°K	65R5
	$a = 4.043 \text{ \AA}$, $b = 4.012 \text{ \AA}$, $\beta = 90^\circ 33'$ at RT.				
3	Crystal structure: Ordered perovskite.				65R5

66

4		
10		
11		
Nr. 1		
1a		
b		
3		
5a		
c		
Nr. 1		
1a		
Nr. 1		
1a		
b		
2a		
3		
5a		
9a		
11		
12b		
c		

4	Lattice distortion: Fig. 359.			65R5
10	Electrical conductivity: $\sigma = 1 \cdot 10^{-1} \Omega^{-1} \text{ m}^{-1}$.			65R5
11	Magnetic susceptibility and magnetic moment: Fig. 360. The linear temperature dependence of χ_{magn}^{-1} with a positive value of $\Theta_{\text{p magn}} = 85^\circ \text{K}$, and the appearing of the spontaneous moment at 103°K , may indicate the presence of ferromagnetic properties in this compound, which is in agreement with the positive sign of the indirect exchange interaction proposed by GOODENOUGH for Mn^{2+} and Re^{3+} ions. However, the magnitudes of the calculated theoretical spontaneous moments agree with the experimental values only on the assumption of an anti-ferromagnetic interaction between ions distributed in an ordered fashion over the octahedral vacancies.			65R5
Nr. 1B3-i $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$				
1a	Ferroelectricity in $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ was discovered by SMOLENSKII et al. in 1959.			59S9
b	phase	II	I	59S9
	state	F	P	
	crystal system	tetragonal ^a) (possibly)	cubic	
	Θ	90 $^\circ \text{C}$		
	$a = (4.074 \pm 0.001) \text{ \AA}$, $c = (4.083 \pm 0.001) \text{ \AA}$ at RT. ^a)			
3	Crystal structure: In the powder patterns, additional to the principal lines of the perovskite structure, superstructural lines were observed indicating a doubling of the lattice period.			59I3
5a	Dielectric constant: Fig. 361.			59S9
c	Spontaneous polarization: $P_s \approx 3.6 \cdot 10^{-2} \text{ cm}^{-2}$ at 18°C .			
Nr. 1B3-ii $\text{Pb}(\text{Mn}_{1/2}\text{Nb}_{1/2})\text{O}_3$				
1a	A synthesis of $\text{Pb}(\text{Mn}_{1/2}\text{Nb}_{1/2})\text{O}_3$ with perovskite structure was reported by VENEV-TSEV et al.			64V3
Nr. 1B3-iii $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$				
1a	Ferroelectricity in $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ was discovered by SMOLENSKII et al. in 1958.			58S4
b	phase	III	II	I
	state	F, A_{magn}	F, P_{magn}	P, P_{magn}
	crystal system	rhombohedral	rhombohedral	cubic
	space group			$\text{Pm}\bar{3}\text{m-O}_h^1$
	Θ	143	387	$^\circ \text{K}$
	$a = 4.014 \text{ \AA}$, $\alpha = 89.92^\circ$ at RT.			62B10
2a	Crystal growth: Flux method with PbO .			62B7
3	Crystal structure: Disordered perovskite; X-ray studies have not shown any ionic ordering in the octahedral sites of perovskite structure. The magnetic peak was found in the neutron diffraction experiments at 78°K . The effective magnetic moment of the Fe^{3+} ion was found to be $(0.80 \pm 0.16) \mu_B$ at 78°K from the calculation of the intensity of the (111) reflection, which is about 90% of the magnetic moment at 0°K . Fig. 362.			64S8 65D6
5a	Dielectric constant: Fig. 363.			
9a	Optical absorption: Fig. 364.			
11	Magnetic susceptibility: Fig. 365. $\mu_{\text{eff}} = 5.4 \mu_B$.			62B7
12b	ESR: Fig. 366.			66S22
c	Mössbauer effect: Fig. 367, 368. The quadrupile splitting $\Delta E_{\text{qu}} = (0.37 \pm 0.02) \text{ mm sec}^{-1}$, the isomer shift $\delta = (0.52 \pm 0.02) \text{ mm sec}^{-1}$, corresponding to trivalent iron (at 20°C).			

1.1.1. Oxides des Perovskit-Typs

Nr. 1B3-iv $\text{Pb}(\text{Co}_{1/2}\text{Nb}_{1/2})\text{O}_3$

1a	A synthesis of $\text{Pb}(\text{Co}_{1/2}\text{Nb}_{1/2})\text{O}_3$ with perovskite structure was reported by VENEV-TSEV et al.	64V3
b	Informations on the dielectric and magnetic properties are available:	65R5

Nr. 1B3-v $\text{Pb}(\text{Ni}_{1/2}\text{Nb}_{1/2})\text{O}_3$

1a	$\text{Pb}(\text{Ni}_{1/2}\text{Nb}_{1/2})\text{O}_3$ with perovskite structure was synthesized by the addition of 5 mol % BaO.	65S17
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Nr. 1B3-vi $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$

1a	Dielectric anomaly in $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ was found by KUPRIYANOV and FESENKO in 1965.	65K9												
b	<table> <tr> <th>phase</th><th>II</th><th>I</th></tr> <tr> <td>state</td><td>(F)</td><td>P</td></tr> <tr> <td>crystal system</td><td>monoclinic (possibly)</td><td>cubic</td></tr> <tr> <td>θ</td><td>90</td><td>$^{\circ}\text{C}$</td></tr> </table> <p>$a = 4.11 \text{ \AA}$ at RT.</p>	phase	II	I	state	(F)	P	crystal system	monoclinic (possibly)	cubic	θ	90	$^{\circ}\text{C}$	65K9
phase	II	I												
state	(F)	P												
crystal system	monoclinic (possibly)	cubic												
θ	90	$^{\circ}\text{C}$												
5a	Dielectric constant: Fig. 369.													

Nr. 1B3-vii $\text{Pb}(\text{Yb}_{1/2}\text{Nb}_{1/2})\text{O}_3$

1a	Antiferroelectric properties in $\text{Pb}(\text{Yb}_{1/2}\text{Nb}_{1/2})\text{O}_3$ were reported by FILIP'EV et al. in 1963.	63F1												
b	<table> <tr> <th>phase</th><th>II</th><th>I</th></tr> <tr> <td>state</td><td>AF</td><td>P</td></tr> <tr> <td>crystal system</td><td>monoclinic</td><td>cubic</td></tr> <tr> <td>θ</td><td>300, 310*</td><td>$^{\circ}\text{C}$</td></tr> </table> <p>$a = 4.168 \text{ \AA}$, $b = 4.107 \text{ \AA}$, $\beta = 90^{\circ} 27'$ at RT*).</p>	phase	II	I	state	AF	P	crystal system	monoclinic	cubic	θ	300, 310*	$^{\circ}\text{C}$	65K9 a) 64T4
phase	II	I												
state	AF	P												
crystal system	monoclinic	cubic												
θ	300, 310*	$^{\circ}\text{C}$												
3	Crystal structure: Superstructure lines, corresponding to ordering of Yb^{3+} and Nb^{5+} ions were found.	64T4												
4	Lattice distortion: Fig. 370. Thermal expansion: Fig. 371.													
5a	Dielectric constant: Fig. 372.													

Nr. 1B3-viii $\text{Pb}(\text{Ho}_{1/2}\text{Nb}_{1/2})\text{O}_3$

1a	Dielectric anomaly in $\text{Pb}(\text{Ho}_{1/2}\text{Nb}_{1/2})\text{O}_3$ was found by KUPRIYANOV and FESENKO.	65K9												
b	<table> <tr> <th>phase</th><th>II</th><th>I</th></tr> <tr> <td>state</td><td>(A)</td><td>P</td></tr> <tr> <td>crystal system</td><td>monoclinic</td><td>cubic</td></tr> <tr> <td>θ</td><td>240</td><td>$^{\circ}\text{C}$</td></tr> </table> <p>$a = 4.160 \text{ \AA}$, $b = 4.106 \text{ \AA}$, $\beta = 90^{\circ} 30'$ at RT.</p>	phase	II	I	state	(A)	P	crystal system	monoclinic	cubic	θ	240	$^{\circ}\text{C}$	65K9
phase	II	I												
state	(A)	P												
crystal system	monoclinic	cubic												
θ	240	$^{\circ}\text{C}$												
5a	Dielectric constant: Fig. 373.													

Nr. 1B3-ix $\text{Pb}(\text{Lu}_{1/2}\text{Nb}_{1/2})\text{O}_3$

1a	Dielectric anomaly in $\text{Pb}(\text{Lu}_{1/2}\text{Nb}_{1/2})\text{O}_3$ was found by SMOLENSKII and AGRANOV-SKAYA in 1958.	58S3
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1b	phase	II	I	65K9
	state	(A)	P	
	crystal system	monoclinic	cubic	
	Θ	270 °C		
	$a = 4.152 \text{ \AA}, b = 4.093 \text{ \AA}, \beta = 90^\circ 30' \text{ at RT.}$			
4	Thermal expansion: Fig. 374.			
5a	Dielectric constant: Fig. 375.			
Nr. 1B3-x Pb(Sc _{1/2} Ta _{1/2})O ₃				
1a	Ferroelectricity in Pb(Sc _{1/2} Ta _{1/2})O ₃ was discussed by SMOLENSKII et al. in 1959.			59S9
b	phase	II	I	59S9 *)59I3
	state	F	P	
	crystal system	tetragonal ^a) (possibly)	cubic	
	Θ	26 °C		
	$a = (4.072 \pm 0.001) \text{ \AA}, c = (4.072 \pm 0.001) \text{ \AA} \text{ at RT}^a$.			
3	Crystal structure: The large number of superstructure lines and their great intensity in Pb(Sc _{1/2} Ta _{1/2})O ₃ indicates that the degree of ordering of Sc ³⁺ and Ta ⁵⁺ ions is greater than in Pb(Sc _{1/2} Nb _{1/2})O ₃ . See 1B3-i-3.			59I3
5a	Dielectric constant: Fig. 376.			
Nr. 1B3-xi Pb(Mn _{1/2} Ta _{1/2})O ₃				
1a	Pb(Mn _{1/2} Ta _{1/2})O ₃ with perovskite structure was synthesized by the addition of 5 mol% SrO.			65S17
Nr. 1B3-xii Pb(Fe _{1/2} Ta _{1/2})O ₃				
1a	Ferroelectricity in Pb(Fe _{1/2} Ta _{1/2})O ₃ was discovered by SMOLENSKII et al. in 1959.			59S7
b	phase	III	II	68N1 *)65S17
	state	F, A _{magn}	F, P _{magn}	
	crystal system	rhombohedral	rhombohedral ^a)	
	space group		Pm3m-O _h	
	Θ	143, 133 ^a)	243, 233 ^a) °K	
	$P_s \parallel [111]$ (probably). $a = (4.007 \pm 0.001) \text{ \AA} \text{ at RT.}$ black (dark orange for thin samples).			
2a	Crystal growth: Flux method with PbO. When the soak temperature is higher than 1200 °C, crystals are obtained having both pyrochloride and perovskite structure.			68N1
3	Crystal structure: Disordered perovskite.			65S17
4	phase	lattice constants		68N1
	I	$a = (4.007 \pm 0.001) \text{ \AA} \text{ at RT.}$		
	II	$a = (4.006 \pm 0.001) \text{ \AA} \text{ at } 90^\circ \text{ K}$ $\alpha = 89.89^\circ \pm 0.02^\circ$		
5a	Dielectric constant: Fig. 377, 378.			
c	Spontaneous polarization: Fig. 379.			
11	Magnetic susceptibility: Fig. 380. $\mu_{\text{eff}} = 5.92 \mu_B; \Theta_{\text{p magn}} = -370^\circ \text{ K.}$			68N1

Series of Perovskite Types

Nr. 1B3-xiii $\text{Pb}(\text{Co}_{1/2}\text{Ta}_{1/2})\text{O}_3$

1a	A synthesis of $\text{Pb}(\text{Co}_{1/2}\text{Ta}_{1/2})\text{O}_3$ with perovskite structure was reported by SHVORNEVA and VENEVTSEV. The compound was stabilized by the addition of 1 mol% La_2O_3 .	65S17
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Nr. 1B3-xiv $\text{Pb}(\text{Yb}_{1/2}\text{Ta}_{1/2})\text{O}_3$

1a	Dielectric anomaly in $\text{Pb}(\text{Yb}_{1/2}\text{Ta}_{1/2})\text{O}_3$ was reported by ISUPOV and KRANIK in 1964.		64I6
b	phase	II	I
	state	(A)	F
	crystal system	monoclinic	cubic
	θ	280, 285*) °C	
	$a = 4.154 \text{ \AA}$, $b = 4.108 \text{ \AA}$, $\beta = 90^\circ 30'$ at RT.		a)65K9
4	Thermal expansion: Fig. 381.		
5a	Dielectric constant: Fig. 382.		

Nr. 1B3-xv $\text{Pb}(\text{Lu}_{1/2}\text{Ta}_{1/2})\text{O}_3$

1a	Dielectric anomaly in $\text{Pb}(\text{Lu}_{1/2}\text{Ta}_{1/2})\text{O}_3$ was found by SMOLENSKII and AGRANOV-SKAYA in 1958.		58S3
b	phase	II	I
	state	(A)	P
	crystal system	monoclinic	cubic
	θ	280 °C	
	$a = 4.153 \text{ \AA}$, $b = 4.107 \text{ \AA}$, $\beta = 90^\circ 30'$ at RT.		65K9
4	Lattice distortion: Fig. 383. Thermal expansion: Fig. 384.		
5	Dielectric constant: Fig. 385.		

Nr. 1B3-xvi $\text{Pb}(\text{Fe}_{1/2}\text{W}_{1/2})\text{O}_3$

1a	A synthesis of $\text{Pb}(\text{Fe}_{1/2}\text{W}_{1/2})\text{O}_3$ with perovskite structure was reported by VENEVTSEV et al.	64V3
b	The magnetic measurements confirmed the presence of the spinel phase in a sample of this composition.	65R5

Nr. 1B3-xvii $\text{Pb}(\text{Li}_{1/4}\text{Nb}_{1/4}\text{W}_{1/2})\text{O}_3$ and sister crystals

1a	Following composite perovskite compounds containing Pb were synthesized:			64V3
	$\text{Pb}(\text{Li}_{1/4}\text{Nb}_{1/4}\text{W}_{1/2})\text{O}_3$	$\text{Pb}(\text{Zn}_{1/4}\text{Mn}_{1/4}\text{Nb}_{1/2})\text{O}_3$	$\text{Pb}(\text{Co}_{1/4}\text{Mn}_{1/4}\text{W}_{1/2})\text{O}_3$	65V3
	$\text{Pb}(\text{Mg}_{1/4}\text{Mn}_{1/4}\text{Nb}_{1/2})\text{O}_3$	$\text{Pb}(\text{Cd}_{1/4}\text{Mn}_{1/4}\text{Nb}_{1/2})\text{O}_3$	$\text{Pb}(\text{Ni}_{1/4}\text{Mn}_{1/4}\text{W}_{1/2})\text{O}_3$	
	$\text{Pb}(\text{Co}_{1/4}\text{Mn}_{1/4}\text{Nb}_{1/2})\text{O}_3$	$\text{Pb}(\text{Mg}_{1/4}\text{Mn}_{1/4}\text{Ta}_{1/2})\text{O}_3$	$\text{Pb}(\text{Cd}_{1/4}\text{Mn}_{1/4}\text{W}_{1/2})\text{O}_3$	
	$\text{Pb}(\text{Ni}_{1/4}\text{Mn}_{1/4}\text{Nb}_{1/2})\text{O}_3$	$\text{Pb}(\text{Mg}_{1/4}\text{Mn}_{1/4}\text{W}_{1/2})\text{O}_3$	$\text{Pb}(\text{Sc}_{1/4}\text{Cr}_{1/4}\text{Nb}_{1/2})\text{O}_3$	

Nr. 1B4-i $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$

1a	Ferroelectricity in $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ was discovered by SMOLENSKII and AGRANOV-SKAYA in 1958.		58S3, 59S6
b	phase	II	I
	state	F	P
	crystal system		cubic
	space group		$\text{Pm}3\text{m}-\text{O}_h$
	θ	265*) °K	
	$\rho = 8.12 \cdot 10^3 \text{ kg m}^{-3}$, $a = 4.04 \text{ \AA}$ at RT. Transparent, pale yellow.		61B5, 60S7 a)67B9 67B18

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2a	Crystal growth: Flux method (using PbO). Kyropoulos method.	59M5 67B18															
3	Crystal structure: Disordered perovskite.	61B5															
4	Thermal expansion: Fig. 386.																
5a	Dielectric constant: Fig. 387, 388, 389.																
b	Nonlinear dielectric properties: $E = [(T - \Theta_p) (\epsilon_0 C)^{-1}] P + \xi P^3 + \zeta P^5 + \dots$, where $\Theta_p = 265^\circ\text{K}$, $C = (3.7 \pm 1.0) \cdot 10^5^\circ\text{K}$, and $\xi \cong 5.6 \cdot 10^8 \text{ V m}^5 \text{ C}^{-3}$.	67B9															
c	Spontaneous polarization and coercive field: Fig. 390.																
7a	Piezoelectricity: Fig. 391.																
9a	Refractive index: $n = 2.56$ for 6328 \AA at 299°K . Birefringence: It was found that the crystals $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ behave like optically isotropic crystals. An applied electric field causes double refraction. Fig. 392.	67B9															
e	Quadratic electrooptic effect: $M_{11} - M_{12} = +0.015 \text{ m}^4 \text{ C}^{-2}$, $M_{44} = +0.008 \text{ m}^4 \text{ C}^{-2}$ for 6328 \AA at 299°K .	67B9															
14a	Domain structure: Clear domains were observed only in very thin wafers (e. g., $20 \cdot 10^{-6} \text{ m}$).	61B5															
Nr. 1B4-ii $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$																	
1a	Ferroelectric $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ crystal was synthesized by Bokov and MYL'NIKOVA in 1960.	60B7															
b	<table border="1"> <tr> <td>phase</td><td>II</td><td>I</td></tr> <tr> <td>state</td><td>F</td><td>P</td></tr> <tr> <td>crystal system</td><td></td><td>cubic</td></tr> <tr> <td>Θ</td><td>140</td><td>$^\circ\text{C}$</td></tr> </table> <p>$a = 4.04 \text{ \AA}$ at RT. light yellow.</p>	phase	II	I	state	F	P	crystal system		cubic	Θ	140	$^\circ\text{C}$	60B7			
phase	II	I															
state	F	P															
crystal system		cubic															
Θ	140	$^\circ\text{C}$															
2a	Crystal growth: Flux method with PbO. The crystals were separated from the matrix solution by washing in acetic acid at RT for a long time.	60B7															
5a	Dielectric constant: Fig. 393.																
Nr. 1B4-iii $\text{Pb}(\text{Cd}_{1/3}\text{Nb}_{2/3})\text{O}_3$																	
1b	Dielectric anomaly in $\text{Pb}(\text{Cd}_{1/3}\text{Nb}_{2/3})\text{O}_3$ was reported by VENEVTSEV et al. in 1966.	65T5, 66V5															
Nr. 1B4-iv $\text{Pb}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3$																	
1a	Ferroelectricity in $\text{Pb}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3$ was found by Bokov and MYL'NIKOVA in 1960.	60B7															
b	<table border="1"> <tr> <td>phase</td><td>II</td><td>I</td></tr> <tr> <td>state</td><td>F</td><td>P</td></tr> <tr> <td>crystal system</td><td></td><td>cubic</td></tr> <tr> <td>space group</td><td></td><td>$\text{Pm}3\text{m-O}_h^1$</td></tr> <tr> <td>Θ</td><td>-98</td><td>$^\circ\text{C}$</td></tr> </table> <p>$a = 4.04 \text{ \AA}$ at RT. brown.</p>	phase	II	I	state	F	P	crystal system		cubic	space group		$\text{Pm}3\text{m-O}_h^1$	Θ	-98	$^\circ\text{C}$	60B7
phase	II	I															
state	F	P															
crystal system		cubic															
space group		$\text{Pm}3\text{m-O}_h^1$															
Θ	-98	$^\circ\text{C}$															
2a	Crystal growth: Flux method with PbO.	60B7															
5a	Dielectric constant: Fig. 394.																

11-1 Cardes des Perovskit-Typs

Nr. 1B4-v $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$

1a	Ferroelectricity in $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ was discovered by SMOLENSKII and AGRANOV-SKAYA in 1958.			58S3, 59S6
b	phase	II	I	61B5, 60S7
	state	F	P	
	crystal system		cubic	
	space group		$\text{Pm}\bar{3}\text{m}-\text{O}_h^1$	
	θ	153	$^{\circ}\text{K}$	
	$a = 4.03 \text{ \AA}$ at RT. $\rho = 8.55 \cdot 10^3 \text{ kg m}^{-3}$. yellowish green.			59M5
2a	Crystal growth: Flux method with PbO .			59M5
3	Crystal structure: Disordered perovskite.			59M5
4	Thermal expansion: Fig. 395.			61B5
5a	Dielectric constant: Fig. 396, 397, 398.			
9a	Birefringence: Fig. 399.			

Nr. 1B4-vi $\text{Pb}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$

1a	Ferroelectricity in $\text{Pb}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ was found by BOKOV and MYL'NIKOVA in 1960.			60B7
b	phase	II	I	60B7
	state	F	P	
	crystal system		cubic	
	space group		$\text{Pm}\bar{3}\text{m}-\text{O}_h^1$	
	θ	-98	$^{\circ}\text{C}$	
	$a = 4.02 \text{ \AA}$ at RT. light yellow.			
2a	Crystal growth: Flux method with PbO .			60B7
3	Crystal structure: Disordered perovskite.			60B7
5a	Dielectric constant: Fig. 400.			

Nr. 1B4-vii $\text{Pb}(\text{Co}_{1/3}\text{Ta}_{2/3})\text{O}_3$

1a	Ferroelectricity in $\text{Pb}(\text{Co}_{1/3}\text{Ta}_{2/3})\text{O}_3$ was found by BOKOV and MYL'NIKOVA in 1960.			60B7
b	phase	II	I	60B7
	state	F	P	
	crystal system		cubic	
	space group		$\text{Pm}\bar{3}\text{m}-\text{O}_h^1$	
	θ	-140	$^{\circ}\text{C}$	
	$a = 4.01 \text{ \AA}$ at RT. brown.			
2a	Crystal growth: Flux method with PbO .			60B7
3	Crystal structure: Disordered perovskite.			60B7
5a	Dielectric constant: Fig. 401.			

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Nr. 1B4-viii Pb(Ni _{1/3} Ta _{2/3})O ₃					
1a	Ferroelectricity in Pb(Ni _{1/3} Ta _{2/3})O ₃ was found by BOKOV and MYL'NIKOVA in 1960.			60B7	
b	phase	II	I	60B7	
	state	F	P		
	crystal system		cubic		
	space group		Pm3m-O _h ¹		
	θ	-180 °C			
	a = 4.01 Å at RT. green.				
2a	Crystal growth: Flux method.			60B7	
3	Crystal structure: Disordered perovskite.			60B7	
5a	Dielectric constant: Fig. 402.				
Nr. 1B5-i Pb(Mn _{2/3} W _{1/3})O ₃					
1a	Dielectric and magnetic anomalies in Pb(Mn _{2/3} W _{1/3})O ₃ were reported by ROGINSKAYA et al. in 1965.			65R5	
b	phase	III	II	I	65R5
	state	(A), (A _{magn})	(A), P _{magn}	P, P _{magn}	
	crystal system		monoclinic	cubic	
	θ	203	473	°K	
	a = c = 4.098 Å, b = 4.014 Å, β = 90° 23' at RT.				
5a	Dielectric constant: Fig. 403.				
10	σ = 2 · 10 ¹¹ Ω ⁻¹ m ⁻¹ .			65R5	
11	Magnetic susceptibility: see Fig. 403. θ _{p magn} = -75 °K.				
Nr. 1B5-ii Pb(Fe _{2/3} W _{1/3})O ₃					
1a	Ferroelectricity in Pb(Fe _{2/3} W _{1/3})O ₃ was discovered by SMOLENSKII et al. in 1959.			59S7	
b	phase	III	II	I	62B7
	state	F, A _{magn}	P, A _{magn}	P, P _{magn}	
	crystal system		cubic	cubic	
	θ	178	363	°K	
	a = 4.02 Å at RT.				
2a	Flux method (PbO).			62B7	
5a	Dielectric constant: Fig. 404.				
11	Magnetic susceptibility: see Fig. 404. Magnetization is a linear function of the magnetic field intensity up to 8000 Oe. Effective magnetic moment: 4.2 μ _B .			62B7	
12b	ESR: Fig. 405.				
1C Solid solutions with perovskite-type oxides as end members					
Nr. 1C-a1 NaNbO ₃ -KNbO ₃					
1b	Phase diagram: Fig. 406, 407, 408. Lattice parameters: Fig. 409.				
5a	Dielectric constant: Fig. 410; see Tab. 60. Polarization and coercive field: Fig. 411.				
6a	Transition energy: Tab. 59.				
7a	Electromechanical properties: Fig. 412 ... 417; Tab. 60.				

Tab. 59. $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$. Transition energy ΔQ_m . [54S3]

x	Lower phase change	Upper phase change
1.00 (KNbO_3)	85 cal/mole	190 cal/mole
0.10	20 cal/mole	60 cal/mole
0 (NaNbO_3)	—	50 cal/mole

Tab. 60. $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ (ceramics). Electric and electromechanical constants. [59E1]

Dielectric constant (100 kHz)	290
Dissipation factor (100 kHz)	$\approx 4.0\%$
Specific resistivity ρ	$10^{10} \Omega \text{ m}$
Density ρ	$4.25 \cdot 10^3 \text{ kg m}^{-3}$
Poisson's ratio (assumed)	0.27
Coupling factor k_p	$0.34 \dots 0.39$
Frequency constant $f_R \tau$	1.67 kHz m
Mechanical Q_{mech} (radial)	130
Young's modulus E	$1.04 \cdot 10^{11} \text{ N m}^{-2}$
Piezoelectric constant $-d_{31}$	$32 \cdot 10^{-12} \text{ C N}^{-1}$
Piezoelectric constant $-g_{31}$	$12.6 \cdot 10^{-3} \text{ m}^2 \text{ C}^{-1}$
Piezoelectric constant d_{33}^*	$80 \cdot 10^{-12} \text{ C N}^{-1}$
Piezoelectric constant g_{33}^*	$31.5 \cdot 10^{-3} \text{ m}^2 \text{ C}^{-1}$
Coupling factor k_{33}^*	0.51

Nr. 1C-a2 $\text{NaNbO}_3\text{-NaTaO}_3$

1b	Phase diagram: Fig. 418. Lattice parameters: Fig. 419.
4	Thermal expansion: Fig. 420.
5a	Dielectric constant: Fig. 421.
9a	Birefringence: Fig. 422.

Nr. 1C-a3 $\text{NaNbO}_3\text{-NaSbO}_3$

1a	Curie temperature: Fig. 423.
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Nr. 1C-a4 $\text{KNbO}_3\text{-KTaO}_3$

1	Phase diagram: Fig. 424, 425.
5a	Dielectric properties: Fig. 426, 427. Θ_f : see Tab. 61.
6	Thermal properties: Fig. 428; Tab. 61.
9	See 1C-a5 for optical properties of $\text{K}(\text{Ta}_{0.35}\text{Nb}_{0.65})\text{O}_3$ (KTN).

Tab. 61. $\text{K}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_3$. L : latent heat, Θ_f : Curie point, A : constant in the formula for free energy = $A(T - \Theta_f)P^2 + \dots$, P_{calc} : P_s calculated for $T = \Theta_f$. [59H1]

x	L cal mol $^{-1}$	Θ_f °K	A 10^5 °K^{-1}	P_{calc} 10^{-2} C m^{-2}
0	110 ± 10	679	2.6	27
0.06	46 ± 4	656	2.7	17.7
0.12	10 ± 2	623	2.85	7.9
0.18	4.0 ± 2	591	3.05	5.1

Nr. 1C-a5 $\text{K}(\text{Ta}_{0.35}\text{Nb}_{0.65})\text{O}_3$ (KTN)For general properties of $\text{KNbO}_3\text{-KTaO}_3$, see 1C-a4.

9b	Electroreflectance: Fig. 429.
d	Faraday rotation: Fig. 430. See also Tab. 44.

Nr. 1C-a6 $\text{CaTiO}_3\text{-SrTiO}_3$

1b	Phase diagram: Fig. 431, 432, 433. Lattice parameters: Fig. 434.
5a	Dielectric constant: Fig. 435, 436.
c	Spontaneous polarization: Fig. 437.

Nr. 1C-a7 $\text{CaTiO}_3\text{-BaTiO}_3$

1b	Phase diagram: Fig. 438, 439, 440. Lattice parameters: Fig. 441.
5a	Dielectric constant: Fig. 442, 443.
6b	Thermal conductivity: Fig. 444.
7a	Electromechanical property: Tab. 62. See Fig. 183 and Tab. 40.

* Estimated values.

Tab. 62. $(\text{Ba}_{1-x}\text{Ca}_x)\text{TiO}_3$ (ceramics, pure BaTiO_3 base). d_{31} and d_{33} at RT. [57B4]

x	ρ 10^3 kg m^{-3}	ρ_x 10^3 kg m^{-3}	d_{31} $10^{-12} \text{ C N}^{-1}$	d_{33} $10^{-12} \text{ C N}^{-1}$	$-d_{33}/d_{31}$	Porosity ($1 - (\rho/\rho_x)$)
0	5.85	6.017	-97.5	229	2.35	0.028
0.05	5.70	5.85	-66.6	167	2.51	0.026
0.07	5.68	5.80	-58.0	150	2.58	0.021
0.09	5.65	5.74	-52.1	139	2.67	0.016
0.12	5.55	5.66	-43.4	124.5	2.88	0.019

Nr. 1C-a8 $\text{CaTiO}_3\text{-PbTiO}_3$ 1b | Curie temperature: Fig. 445.
Lattice parameter: Fig. 446.Nr. 1C-a9 $\text{SrTiO}_3\text{-BaTiO}_3$ 1b | Phase diagram: Fig. 447 ... 450.
Lattice parameter: Fig. 451; see Fig. 448.5a | Dielectric constant: Fig. 452.
Microwave dielectric loss: Tab. 63.

6a | Specific heat: Fig. 453.

10b | Conductivity associated with doping: Fig. 454, 455, 456.

Tab. 63. $(\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3$. Dielectric loss: α, β, γ at 20 GHz. [62R4]. $(T - \Theta_p) \tan \delta = \alpha + \beta T + \gamma T^2$.

Sample		Heat treatment	Grain size μ	Θ_p $^\circ\text{K}$	α $^\circ\text{K}$	$\beta \cdot 10^4$	$\gamma \cdot 10^4$ ($^\circ\text{K}$) $^{-1}$
Polycrystalline	SrTiO_3	Hot pressed and fired in air at 900 $^\circ\text{C}$ for 10 h	1	37	0.33	7.7	4.3
		Refired at 1200 $^\circ\text{C}$ in air for 10 h	3	37	0.26	5.5	4.7
		Refired at 1400 $^\circ\text{C}$ in air for 10 h	15	37	0.17	4.4	4.2
		Refired at 1500 $^\circ\text{C}$ in O_2 for 6 h	30	37	0.08	4.5	3.7
	$\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$	Hot pressed and fired in O_2 at 1500 $^\circ\text{C}$ for 10 h	30	105	0.6	9	2.5
	$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$	Hot pressed and fired in O_2 at 1500 $^\circ\text{C}$ for 10 h	30	218	2.0	(9) ^{a)}	(2.5)
	$\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$	Ceramic fired to 1375 $^\circ\text{C}$ in air for 1 h	8	280	2.2	(9)	(2.5)
Single crystal	$\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$	Ceramic fired to 1300 $^\circ\text{C}$ in air for 1 h	8	324	1.6	(9)	(2.5)
	SrTiO_3	None	∞	37	0	6.53	2.54
	$\text{SrTiO}_3 + 0.1\% \text{ Gd}^{3+}$	None	∞	37	0.033	(6.53)	(2.54)
	$\text{SrTiO}_3 + 0.03\% \text{ Fe}^{3+}$	None	∞	37	0.043	(6.53)	(2.54)

Nr. 1C-a10 $\text{SrTiO}_3\text{-PbTiO}_3$ 1b | Curie temperature: Fig. 457.
Lattice parameter: Fig. 458.5a | Dielectric constant: Fig. 459.
Curie constant: Fig. 460.

6a | Transition heat: Fig. 461.

Nr. 1C-a11 $\text{BaTiO}_3\text{-PbTiO}_3$ 1b | Phase diagram: Fig. 462.
Lattice parameter: Fig. 463.

5a | Dielectric constant: Fig. 464.

6a | Specific heat: Fig. 465.
Transition heat: Fig. 466.

7 | Electromechanical properties: see 1A-8.

16 | Radiation damage: Fig. 467.

^{a)} Values in parentheses indicate that these values were assumed in order to determine α .

Nr. 1C-a12 $\text{CaZrO}_3\text{-BaZrO}_3$

1b | Lattice parameter: Fig. 468.

Nr. 1C-a13 $\text{CaZrO}_3\text{-PbZrO}_3$

1b | Phase diagram: Fig. 469.

4 | Thermal expansion: Fig. 470.

5a | Dielectric constant: Fig. 471.

Nr. 1C-a14 $\text{SrZrO}_3\text{-PbZrO}_3$ 1b | Phase diagram: Fig. 472, 473.
Lattice parameter: Fig. 474.

4 | Thermal expansion: Fig. 475, 476, 477; Tab. 64.

5a | Dielectric constant: Fig. 478, 479.

c | Polarization: Fig. 480.

6a | Specific heat: Fig. 481.
Transition heat: Tab. 65.Tab. 64. PbZrO_3 , $(\text{Pb}_{0.95}\text{Sr}_{0.05})\text{ZrO}_3$, and $(\text{Pb}_{0.925}\text{Ba}_{0.075})\text{ZrO}_3$. $\Delta V/V$. ΔV : anomalous volume change at the transition point. [54S2]

Composition	$\Delta V/V [10^{-4}]$	
	Lowest phase	Intermediate phase
PbZrO_3	-41 at 230 °C	—
$(\text{Pb}_{0.925}\text{Ba}_{0.075})\text{ZrO}_3$	-43 at 150 °C	+24 at 190 °C
$(\text{Pb}_{0.95}\text{Sr}_{0.05})\text{ZrO}_3$	-30 at 210 °C	-20 at 230 °C

Tab. 65. PbZrO_3 , $(\text{Pb}_{0.95}\text{Sr}_{0.05})\text{ZrO}_3$, and $(\text{Pb}_{0.925}\text{Ba}_{0.075})\text{ZrO}_3$. ΔQ_m . [52S2]

Composition	$\Delta Q_m [\text{cal mol}^{-1}]$	
	Lower transition	Upper transition
PbZrO_3	—	440
$(\text{Pb}_{0.925}\text{Ba}_{0.075})\text{ZrO}_3$	190	230
$(\text{Pb}_{0.95}\text{Sr}_{0.05})\text{ZrO}_3$	180	230

Nr. 1C-a15 $\text{BaZrO}_3\text{-PbZrO}_3$ 1b | Phase diagram: Fig. 482.
Lattice parameter: Fig. 483.

4 | Thermal expansion: Fig. 484.

5a | Dielectric constant: Fig. 485 ... 488.

c | Coercive field: Fig. 489.

8 | Elastic properties: Fig. 490.

Nr. 1C-a16 $\text{CaHfO}_3\text{-PbHfO}_3$

1b | Phase diagram: Fig. 491.

5a | Dielectric constant: Fig. 492.

Nr. 1C-a17 $\text{SrHfO}_3\text{-PbHfO}_3$

1b | Phase diagram: Fig. 493.

5a | Dielectric constant: Fig. 494.

Nr. 1C-a18 $\text{BaHfO}_3\text{-PbHfO}_3$

1b | Phase diagram: Fig. 495.

Nr. 1C-a19 $\text{CaSnO}_3\text{-SrSnO}_3$

1b | Lattice parameter: Fig. 496.

Nr. 1C-a20 $\text{BaSnO}_3\text{-SrSnO}_3$

1b | Lattice parameter: see Fig. 496.

Nr. 1C-a21 $\text{BaSnO}_3\text{-PbO:SnO}_2$

1b | Phase diagram: Fig. 497.

5a | Dielectric constant: Fig. 498.

Nr. 1C-a22 $\text{CaTiO}_3\text{-CaZrO}_3$

1b | Lattice parameter: Fig. 499.

Nr. 1C-a23 BaTiO ₃ -BaZrO ₃	1b	Phase diagram: Fig. 500. Lattice parameter: Fig. 501.	
	2a	Phase diagram: Fig. 502.	
	5a	Dielectric constant: Fig. 503.	
	8a	Elastic property: Fig. 504	
Nr. 1C-a24 BaTiO ₃ -BaHfO ₃	1b	Phase diagram: Fig. 505. Lattice parameter: Fig. 506.	
	5a	Dielectric constant: Fig. 507.	
Nr. 1C-a25 BaTiO ₃ -BaSnO ₃	1b	Phase diagram: Fig. 508. See also	59I2
	2a	Phase diagram: Fig. 509.	
	4	Thermal expansion: Fig. 510.	
	5a	Dielectric constant: Fig. 511.	
Nr. 1C-a26 BaTiO ₃ -BaUO ₃	1b	Lattice parameter: Fig. 512.	
Nr. 1C-a27 PbTiO ₃ -PbZrO ₃ Pb(Zr _x Ti _{1-x})O ₃ with $x = 0.5 \dots 0.6$; for electromechanical properties of these very important piezo-electric materials, see 1C-a28.			
1a	Ferro- and antiferroelectric phase transitions in the PbTiO ₃ -PbZrO ₃ system were revealed in 1952 by SHIRANE, SUZUKI and TAKEDA.		52S6, 52S4, 52S3
b	Phase diagram at high temperature: Fig. 513. Phase diagram: Fig. 514, 515. Lattice parameter: Fig. 516, 517.		
2	Flux method:		62I1, 64F6, 67F7
4	Lattice distortion: Fig. 518a, b, 519. Thermal expansion: Fig. 520, 521, 522.		
5a	Dielectric constant: Fig. 523 ... 526.		
c	Spontaneous polarization: Fig. 527. Critical field: Fig. 528.		
6	Specific heat: Fig. 529, 530. Transition energy: Tab. 66.		
7 } 8 }	Electromechanical properties: see 1C-a28.		
9	Birefringence: Fig. 531a, b, c.		
16	Radiation damage: Fig. 532.		

Tab. 66. Pb(Zr-Ti)O₃. Transition energy and entropy. [53S1]. x : atomic percent of PbTiO₃; $d\theta/dx$: shift of the transition temperature with x ; $dS(d\theta/dx)$: it may be assumed that the free energy should decrease with the rate of $dS(d\theta/dx)$ with increasing x .

Kind of the phase change	θ °C	ΔQ_m cal mol ⁻¹	ΔS_m cal mol ⁻¹ °K ⁻¹	$d\theta/dx$	$dS(d\theta/dx)$
A _{α} → P _{α}	230 > T > 225	400	0.8	—	(-5.8)
A _{α} → A _{β}	225	110	0.22	-16	-3.5
A _{β} → P _{α}	230	290	0.58	-4	-2.3
A _{α} → F _{α}	240	—	—	-19	—
F _{α} → P _{α}	217	250	0.51	+ 1.0	+0.5
A _{β} → F _{α}	—	40	0.08	—	—

Nr. 1C-a28 $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ($x = 0.5 \dots 0.6$, lead zirconate-titanate)
For general properties of PbTiO_3 - PbZrO_3 see 1C-a27.

1a	JAFÉ, ROTH, and MARZULLO discovered the excellent piezoelectric performances of Pb(Zr-Ti)O ₃ ceramics in 1954. PZT is the trade mark of this substance developed by Clevite Corporation, Cleveland, Ohio, USA.										54J1	
5a	Dielectric constants: Fig. 533 and Fig. 539, 540, 541, 543, 544.											
7) 8)	Electromechanical properties (ceramics): Tab. 67; Fig. 534 ... 538; Tab. 68 ... 72; Fig. 539 ... 542; Tab. 73; Fig. 543 ... 554.											
10	Electrical conductivity: see For breakdown, see										63G1, 61S14 59G2	
Tab. 67. Pb(Ti _{1-x} Zr _x)O ₃ [x = 0.48 ... 0.60] (ceramics). Electromechanical constants at RT. [60B3]												
Zr/Ti atom ratio	k ₃₁	k _p	k ₁₅	k ₃₃	κ ₁₁ ^T	κ ₁₁ ^S	κ ₃₃ ^T	κ ₃₃ ^S obs	κ ₃₃ ^S calc			
48/52	0.170	0.289	0.408	0.435	663	551	666	540	537			
50/50	0.230	0.397	0.504	0.546	855	631	846	585	585			
52/48	0.313	0.529	0.694	0.670	1180	612	730	399	389			
54/46	0.280	0.470	0.701	0.626	990	504	450	253	268			
56/44	0.267	0.450	0.657	0.619	840	477	423	246	258			
58/42	0.254	0.428	0.646	0.607	751	437	397	243	246			
60/40	0.238	0.400	0.625	0.585	672	410	376	240	245			
	s ₁₁ ^E	s ₁₁ ^D	s ₃₃ ^E	s ₃₃ ^D	s ₄₄ ^E	s ₄₄ ^D	s ₆₆	s ₁₂ ^E	s ₁₂ ^D	s ₁₃ ^E	s ₁₃ ^D	Density ρ
	10 ⁻¹² m ² N ⁻¹											10 ³ kgm ⁻³
48/52	10.8	10.5	10.9	8.83	28.3	23.6	28.3	-3.35	-3.66	-3.21	-2.40	7.59
50/50	12.4	11.7	13.3	9.35	32.8	24.5	32.9	-4.06	-4.72	-4.22	-2.60	7.55
52/48	13.8	12.4	17.1	9.35	48.2	25.0	38.4	-4.07	-5.38	-5.80	-2.56	7.55
54/46	11.6	10.7	14.8	9.0	45.0	22.9	29.9	-3.33	-4.24	-4.97	-2.68	7.62
56/44	11.0	10.2	14.0	8.65	39.8	22.6	28.4	-3.22	-4.01	-4.63	-2.57	7.59
58/42	10.5	9.85	12.8	8.10	37.7	21.9	27.1	-3.07	-3.75	-4.12	-2.33	7.64
60/40	10.4	9.75	12.05	7.92	36.9	22.5	26.7	-2.96	-3.55	-3.72	-2.17	7.60
	g ₃₁	g ₃₃	g ₁₅	g ₃₃ - g ₃₁	d ₃₁	d ₃₃	d ₁₅	d ₃₃ - d ₃₁	s ₃₃ ^D + s ₁₁ ^D - 2s ₁₃ ^D			
	10 ⁻³ m ² C ⁻¹				10 ⁻¹² C N ⁻¹				10 ⁻¹² m ² N ⁻¹			
48/52	- 7.3	18.7	28.4	26.0	43.0	110	166	153	24.1			
50/50	- 9.35	23.1	33.2	32.4	70.0	173	251	243	26.2			
52/48	-14.5	34.5	47.2	49.0	93.5	223	494	316	26.9			
54/46	-15.1	38.1	50.3	53.2	60.2	152	440	212	25.1			
56/44	-14.5	37.8	48.0	52.3	54.3	142	357	196	24.0			
58/42	-13.9	36.7	48.8	50.6	48.9	129	325	178	22.6			
60/40	-13.3	35.2	49.3	48.5	44.2	117	293	161	22.0			
	Q _{mech}	Q _E (=1/ tan δ)	P	c ₃₃ ^D	-s ₁₂ ^E	-s ₁₂ ^D	-s ₁₃ ^E	-s ₁₃ ^D				
			10 ⁻² C m ⁻²	10 ¹⁰ N m ⁻²	s ₁₁ ^E	s ₁₁ ^D	√s ₃₃ ^E s ₁₁ ^E	√s ₃₃ ^D s ₁₁ ^D				
48/52	1170	380	17	14.0	0.310	0.349	0.296	0.250				
50/50	950	370	27	13.5	0.328	0.404	0.329	0.249				
52/48	860	360	36	13.4	0.295	0.434	0.376	0.238				
54/46	680	300	42.5	14.8	0.288	0.396	0.380	0.273				
56/44	490	190	48	15.3	0.293	0.394	0.373	0.274				
58/42	500	200	43	15.8	0.292	0.381	0.355	0.261				
60/40	600	210	33	15.6	0.285	0.365	0.332	0.247				

Tab. 68. $(\text{Pb}_{1-x}\text{Sr}_x)(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ and $(\text{Pb}_{1-x}\text{Ca}_x)(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ (modified ceramics). Effects of Ca and Sr on electromechanical properties. [59K4]

Intended composition	ϵ_a 10^3 kgm^{-3}	κ at 1 kHz	24 hours after poling						Θ_f $^\circ\text{C}$
			κ at 1 kHz	$\tan \delta$ % at 1 kHz	k_p	d_{31} 10^{-12} CN^{-1}	g_{31} 10^{-3} m^2C^{-1}	$(s_{11}^E)^{-1}$ 10^{10} Nm^{-2}	
$\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$	7.40	736	544	0.5	0.48	71	14.7	7.67	385
$\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$	7.39	707	542	0.4	0.47	69	14.4	7.76	
$\text{Pb}_{0.99}\text{Ca}_{0.01}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$	7.42	729	624	0.5	0.49	77	13.9	7.89	
$\text{Pb}_{0.99}\text{Sr}_{0.01}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$	7.42	755	584	0.6	0.49	75	14.5	7.68	
$\text{Pb}_{0.95}\text{Ca}_{0.05}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$	7.26	832	973	0.5	0.44	88	10.2	7.62	
$\text{Pb}_{0.95}\text{Sr}_{0.05}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$	7.47	920	1002	0.4	0.50	101	11.4	7.65	360
$\text{Pb}_{0.92}\text{Ca}_{0.08}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$	6.86	794	888	0.4	0.32	60	7.6	7.85	
$\text{Pb}_{0.925}\text{Sr}_{0.075}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$	7.29	942	1094	0.3	0.50	103	10.6	7.94	
$\text{Pb}_{0.90}\text{Sr}_{0.10}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$	7.22	997	1129	0.3	0.49	103	10.3	7.95	290
$\text{Pb}_{0.875}\text{Sr}_{0.125}(\text{Zr}_{0.47}\text{Ti}_{0.53})\text{O}_3$	7.09	609	663	0.3	0.28	40	6.8	9.91	
$\text{Pb}_{0.875}\text{Sr}_{0.125}(\text{Zr}_{0.50}\text{Ti}_{0.50})\text{O}_3$	7.11	813	880	0.3	0.33	57	7.3	9.05	
$\text{Pb}_{0.875}\text{Sr}_{0.125}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$	7.10	973	1149	0.3	0.44	91	9.0	8.32	
$\text{Pb}_{0.875}\text{Sr}_{0.125}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$	7.14	1076	1237	0.4	0.47	100	9.1	8.06	265
$\text{Pb}_{0.875}\text{Sr}_{0.125}(\text{Zr}_{0.54}\text{Ti}_{0.46})\text{O}_3$	7.16	1095	1325	0.6	0.51	119	10.1	7.51	
$\text{Pb}_{0.875}\text{Sr}_{0.125}(\text{Zr}_{0.56}\text{Ti}_{0.44})\text{O}_3$	7.14	1105	1210	0.4	0.51	116	10.8	7.31	
$\text{Pb}_{0.875}\text{Sr}_{0.125}(\text{Zr}_{0.59}\text{Ti}_{0.41})\text{O}_3$	7.17	919	585	0.4	0.45	66	12.7	8.39	
$\text{Pb}_{0.85}\text{Sr}_{0.15}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$	6.90	1106	1260	0.5	0.43	97	8.7	7.68	242
$\text{Pb}_{0.80}\text{Sr}_{0.20}(\text{Zr}_{0.50}\text{Ti}_{0.50})\text{O}_3$	6.56	941	970	0.6	0.29	56	6.5	8.11	
$\text{Pb}_{0.80}\text{Sr}_{0.20}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$	6.48	1212	1257	0.5	0.34	86	7.8	7.05	
$\text{Pb}_{0.80}\text{Sr}_{0.20}(\text{Zr}_{0.54}\text{Ti}_{0.46})\text{O}_3$	6.36	1182	1341	0.8	0.35	91	7.7	6.18	
$\text{Pb}_{0.80}\text{Sr}_{0.20}(\text{Zr}_{0.55}\text{Ti}_{0.45})\text{O}_3$	6.36	1200	1337	0.8	0.34	86	7.3	6.42	
$\text{Pb}_{0.80}\text{Sr}_{0.20}(\text{Zr}_{0.56}\text{Ti}_{0.44})\text{O}_3$	6.35	1107	1113	0.7	0.35	81	8.2	6.50	

Tab. 69. $\text{Pb}(\text{Zr-Ti})\text{O}_3$ (ceramics, modified). Electromechanical properties of $\text{Pb}(\text{Zr}_{0.54}\text{Ti}_{0.46})\text{O}_3$ with five-valent additives. [59K5]. $f_R \cdot r$: radial frequency constant

Addition wt. %	ϵ_a 10^3 kgm^{-3}	Before poling		24 hours after poling						Θ_f $^\circ\text{C}$
		κ at 1 kHz	$\tan \delta$ % at 1 kHz	κ at 1 kHz	$\tan \delta$ % at 1 kHz	k_p	$f_R \cdot r$ $\text{Hz} \cdot \text{m}$	d_{31} 10^{-12} CN^{-1}	Q_{mech}	
None	7.41	707	0.3	537	0.4	0.49	1641	71		390
None	7.29	706	0.4	513	0.5	0.50	1687	69		387
0.1 Nb_2O_5	7.26	598	0.3	508	0.4	0.38	1643	54		
0.5 Nb_2O_5	6.96	732	2.1	790	2.0	0.46	1443	94		
0.8 Nb_2O_5	7.36	965	1.6	1166	1.5	0.48	1606	105		
1.0 Nb_2O_5	7.36	1064	1.8	1308	1.6	0.53	1563	126	61	
1.0 Nb_2O_5	7.60	1055	2.2	1242	2.2	0.54	1538	125		361
1.2 Nb_2O_5	7.34	1011	2.0	1167	1.7	0.48	1614	104	70	
1.4 Nb_2O_5	7.37	1057	2.2	1218	1.9	0.50	1584	113	69	
1.7 Nb_2O_5	7.39	1058	2.0	1218	1.8	0.47	1594	105		
2.0 Nb_2O_5	7.37	1074	2.1	1202	2.0	0.50	1550	115		344
0.5 Nb_2O_5	7.39	1169	2.1	1377	2.0	0.57	1491	146	48	369
0.5 La_2O_3										
1.0 Ta_2O_5	7.31	989	1.5	1187	1.5	0.49	1563	111	61	
1.0 Ta_2O_5	7.22	918	2.0	1121	2.1	0.50	1525	114		368
2.0 Ta_2O_5	7.49	1062	2.2	1230	2.1	0.50	1547	115		
2.0 Ta_2O_5	7.40	1077	1.8	1275	1.8	0.48	1581	111		364
2.5 Ta_2O_5	7.23	959	2.7	1112	2.4	0.36	1518	82	28	
5.0 Ta_2O_5	6.75	995	2.5	1052	2.6	0.33	1508	76		

Tab. 70. $\text{Pb}(\text{Zr-Ti})\text{O}_3$ (ceramics, modified). Electromechanical properties of $\text{Pb}(\text{Zr}_{0.54}\text{Ti}_{0.46})\text{O}_3$ with three-valent additives. [59K5]. $f_R \cdot r$: radial frequency constant

Addition wt. %	ϵ_a 10^3 kgm^{-3}	Before poling		24 hours after poling					Θ_f $^\circ\text{C}$
		κ at 1 kHz	$\tan \delta$ % at 1 kHz	κ at 1 kHz	$\tan \delta$ % at 1 kHz	k_p	$f_R \cdot r$ $\text{Hz} \cdot \text{m}$	d_{31} 10^{-12} CN^{-1}	
None	7.41	707	0.3	537	0.4	0.49	1641	71	390
None	7.29	706	0.4	513	0.5	0.50	1687	69	387
1.0 Y_2O_3	7.26	796	0.9	841	1.0	0.34	1547	66	374
1.0 La_2O_3	7.46	1187	1.9	1483	2.0	0.53	1510	138	
1.0 La_2O_3	7.47	1139	2.2	1387	2.1	0.52	1522	130	339
1.0 Nd_2O_3	7.43	1111	1.6	1395	1.8	0.49	1512	123	
1.0 Nd_2O_3	7.37	1101	1.9	1354	1.8	0.48	1511	119	348
1.0 didymia	7.41	1122	2.2	1341	2.2	0.50	1499	125	
2.0 La_2O_3	7.49	1296	2.6	1545	2.3	0.51	1545	132	
1.0 La_2O_3	7.20	1375	2.1	1792	1.7	0.51	1528	147	
1.0 Nd_2O_3	7.35	1362	2.2	1776	1.9	0.49	1558	136	
0.1 La_2O_3	6.75	790	0.4	870	0.6	0.42	1505	88	
0.2 La_2O_3	6.45	686	0.7	735	0.9	0.37	1419	78	
0.4 La_2O_3	6.44	942	1.4	1100	1.5	0.42	1407	109	
0.8 La_2O_3	7.19	1288	1.8	1682	1.8	0.49	1516	139	
1.0 La_2O_3	7.50	1255	2.4	1532	2.4	0.50	1550	128	

Tab. 71. Electromechanical properties of $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (ceramics), modified with additives of 1 wt% Nb. [59K5]. $f_R \cdot r$: radial frequency constant

Base composition	ϵ_a 10^3 kgm^{-3}	Before poling		24 hours after poling					
		κ at 1 kHz	$\tan \delta$ % at 1 kHz	κ at 1 kHz	$\tan \delta$ % at 1 kHz	k_p	$f_R \cdot r$ $\text{Hz} \cdot \text{m}$	d_{31} 10^{-12} CN^{-1}	Q_{mech}
$\text{Pb}(\text{Zr}_{0.50}\text{Ti}_{0.50})\text{O}_3$	7.38	879	1.5	1041	1.2	0.42	1696	82	81
$\text{Pb}(\text{Zr}_{0.51}\text{Ti}_{0.49})\text{O}_3$	7.31	975	1.6	1188	1.3	0.45	1642	97	73
$\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$	7.39	985	1.5	1200	1.4	0.45	1640	97	76
$\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$	7.43	1092	1.8	1371	1.4	0.53	1547	130	61
$\text{Pb}(\text{Zr}_{0.54}\text{Ti}_{0.46})\text{O}_3$	7.44	1051	1.8	1296	1.7	0.54	1549	128	62
$\text{Pb}(\text{Zr}_{0.55}\text{Ti}_{0.45})\text{O}_3$	7.40	955	2.4	973	2.0	0.56	1524	117	55
$\text{Pb}(\text{Zr}_{0.56}\text{Ti}_{0.44})\text{O}_3$	7.38	818	2.8	745	2.5	0.53	1601	93	56
$\text{Pb}(\text{Zr}_{0.57}\text{Ti}_{0.43})\text{O}_3$	7.41	750	3.0	684	2.5	0.50	1636	82	60
$\text{Pb}(\text{Zr}_{0.58}\text{Ti}_{0.42})\text{O}_3$	7.41	713	3.0	630	2.8	0.49	1676	75	62

Tab. 72. Electromechanical properties of $(\text{Pb}_{0.95}\text{Sr}_{0.05})(\text{Zr}_{0.54}\text{Ti}_{0.46})\text{O}_3$ (ceramics) with Nb_2O_5 or Ta_2O_5 . [59K5]. $f_R \cdot r$: radial frequency constant

Addition wt. %	ϵ_a 10^3 kgm^{-3}	Before poling		24 hours after poling					Θ_f $^\circ\text{C}$
		κ at 1 kHz	$\tan \delta$ % at 1 kHz	κ at 1 kHz	$\tan \delta$ % at 1 kHz	k_p	$f_R \cdot r$ $\text{Hz} \cdot \text{m}$	d_{31} 10^{-12} CN^{-1}	
1.0 Nb_2O_5	7.34	1291	2.0	1609	2.0	0.56	1512	153	306
2.0 Nb_2O_5	7.22	1380	2.4	1662	2.1	0.47	1562	127	
3.0 Nb_2O_5	6.63	1125	2.1	1301	2.1	0.36	1550	91	
2.0 Ta_2O_5	7.33	1343	2.3	1695	2.0	0.54	1517	151	296

Tab. 73. PZT (commercial modified ceramics). Electromechanical constants at RT. [666]

Substance	κ_{11}^T	κ_{11}^S	κ_{33}^T	κ_{33}^S	$10^{-12} \text{ C N}^{-1}$				C m^{-2}				$10^{-3} \text{ m}^2 \text{ C}^{-1}$				h_{15}				
					d_{15}	d_{31}	d_{33}	k_p	k_{33}	k_{31}	k_{15}	h_{33}	s_{11}^E	s_{11}^D	s_{33}^E	s_{33}^D		s_{12}^E	s_{12}^D	s_{13}^E	s_{13}^D
PZT-2	990	504	450	260	440	60.2	152	—	9.8	1.86	9.0	50.3	15.1	38.1	21.9						
PZT-4	1475	730	1300	635	496	—	289	—	12.7	—	15.1	39.4	—	26.1	19.7						
PZT-5A	1730	916	1700	830	584	—	374	—	12.3	—	15.8	38.2	—	24.8	15.2						
PZT-5H	3130	1700	3400	1470	741	—	593	—	17.0	—	23.3	26.8	—	19.7	11.3						
PZT-6A	—	—	1100	—	—	—	195	—	—	—	—	—	—	17.0	—						
PZT-6B	515	441	500	420	135	—	76	—	4.8	—	7.4	29.6	—	17.3	12.2						
PZT-7A	840	450	425	235	368	—	153	—	9.3	—	9.7	49.5	—	40.7	23.4						
PZT-8	—	—	1000	—	—	—	215	—	—	—	—	—	—	24.5	—						
$10^{-12} \text{ N C}^{-1}$																					
PZT-2	—	8.1	39.2	0.28	0.626	0.47	11.6	0.47	10.7	14.8	9.0	—	—	—	—	—	—	—			
PZT-4	—	9.2	26.8	0.334	0.70	0.58	12.3	0.58	10.9	15.5	7.90	—	—	—	—	—	—	—			
PZT-5A	—	7.3	21.5	0.344	0.705	0.60	16.4	0.60	14.4	18.8	9.46	—	—	—	—	—	—	—			
PZT-5H	—	5.05	18.0	0.388	0.752	0.65	16.5	0.65	14.05	20.7	8.99	—	—	—	—	—	—	—			
PZT-6A	—	—	—	0.229	0.54	0.39	11.5	0.39	10.9	—	—	—	—	—	—	—	—	—			
PZT-6B	—	2.6	19.9	0.145	0.375	0.25	9.0	0.25	8.8	9.35	8.05	—	—	—	—	—	—	—			
PZT-7A	—	10.4	46.6	0.306	0.67	0.52	10.7	0.52	9.7	13.9	7.65	—	—	—	—	—	—	—			
PZT-8	—	—	—	0.295	0.60	0.50	11.1	0.50	10.1	13.9	8.9	—	—	—	—	—	—	—			
$10^{-12} \text{ m}^2 \text{ N}^{-1}$																					
PZT-2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—			
PZT-4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—			
PZT-5A	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—			
PZT-5H	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—			
PZT-6A	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—			
PZT-6B	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—			
PZT-7A	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—			
PZT-8	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—			

r Ta₂O₅

%Nb.

Q_{mech}

ith

θ_f
°C90
187
174

339

348

306

296

Nr. 1C-a29 $\text{PbTiO}_3\text{-PbHfO}_3$	1b	Phase diagram: Fig. 555, 556
Nr. 1C-a30 $\text{PbTiO}_3\text{-PbO:SnO}_2$	1b	Phase diagram: Fig. 557.
	5a	Dielectric constant: Fig. 558.
Nr. 1C-a31 $\text{PbZrO}_3\text{-PbHfO}_3$	1b	Phase diagram: Fig. 559.
Nr. 1C-a32 $\text{PbZrO}_3\text{-PbO:SnO}_2$	1b	Phase diagram: Fig. 560. Lattice parameter: Fig. 561.
	4	Thermal expansion: Fig. 562, 563.
	5a	Dielectric constant: Fig. 564a, b.
Nr. 1C-a33 $\text{LaFeO}_3\text{-BiFeO}_3$	1b	Phase diagram: Fig. 565. Lattice parameter: Fig. 566a, b.
	5a	Dielectric constant: Fig. 567.
	11	Magnetization: see Fig. 565.
Nr. 1C-b1 $\text{NaNbO}_3\text{-KTaO}_3$	1b	Phase diagram: Fig. 568. Lattice parameter: Fig. 569.
	4	Thermal expansion: Fig. 570.
	5a	Dielectric constant: Fig. 571.
Nr. 1C-b2 $\text{NaNbO}_3\text{-KSbO}_3$	1a	Curie temperature: see Fig. 423.
Nr. 1C-b3 $\text{BaTiO}_3\text{-PbZrO}_3$	4	Thermal expansion: Fig. 572.
	5a	Dielectric constant: Fig. 573.
Nr. 1C-b4 $\text{BaTiO}_3\text{-PbO:SnO}_2$	1b	Phase diagram: Fig. 574.
	5a	Dielectric constant: Fig. 575.
Nr. 1C-b5 $\text{PbTiO}_3\text{-CaZrO}_3$	1b	Phase diagram: Fig. 576. Lattice parameter: Fig. 577.
	5a	Dielectric constant: Fig. 578.
Nr. 1C-b6 $\text{PbTiO}_3\text{-CaSnO}_3$	1b	Phase diagram: see Fig. 576. Lattice parameter: Fig. 579.
	5a	Dielectric constant: Fig. 580.
Nr. 1C-b7 $\text{PbTiO}_3\text{-SrZrO}_3$	1b	Phase diagram: Fig. 581. Lattice parameter: Fig. 582a, b.
	5a	Dielectric constant: Fig. 583.
Nr. 1C-b8 $\text{PbTiO}_3\text{-SrSnO}_3$	1b	Phase diagram: Fig. 584. Lattice parameter: Fig. 585a, b.
	5a	Dielectric constant: Fig. 586.
Nr. 1C-b9 $\text{PbTiO}_3\text{-BaZrO}_3$	1b	Phase diagram: Fig. 587. Lattice parameter: Fig. 588a, b.
	5a	Dielectric constant: Fig. 589.
	7a	Electromechanical property: Tab. 74.

Tab. 74. $(1-x)\text{PbTiO}_3 - x\text{BaZrO}_3$ (ceramics). k_p and d_{33} at RT. [63B15]

x	Poling field $\cdot 10^5 \text{ V m}^{-1}$ [T in $^\circ\text{C}$]	k_p	d_{33} $\cdot 10^{-12} \text{ C N}^{-1}$
0.25	29 [185 ... 40]	0.16	40
0.30	27 [170 ... 40]	0.23	50
0.35	39 [145 ... 40]	0.30	110
0.40	30 [120 ... 40]	0.17	45

Nr. 1C-b10 $\text{PbTiO}_3\text{-BaSnO}_3$	1b	Phase diagram: Fig. 590. Lattice parameter: Fig. 591a, b.
Nr. 1C-b11 $\text{LaAlO}_3\text{-BiFeO}_3$	1b	Phase diagram: Fig. 592. Lattice parameter: Fig. 593.
	5a	Dielectric constant: Fig. 594.
Nr. 1C-b12 $\text{LaCrO}_3\text{-BiFeO}_3$	1b	Phase diagram: Fig. 595. Lattice parameter: Fig. 596a, b.
	4	Thermal expansion: Fig. 597.
	11	Spontaneous magnetization: see Fig. 595.
Nr. 1C-c1 $\text{NaNbO}_3\text{-CaTiO}_3$	1b	Phase diagram: Fig. 598.
	5a	Dielectric constant: Fig. 599.
Nr. 1C-c2 $\text{NaNbO}_3\text{-BaTiO}_3$	1b	Phase diagram: Fig. 600.
Nr. 1C-c3 $\text{NaNbO}_3\text{-PbTiO}_3$	1b	Transition temperature: Fig. 601.
	5a	Dielectric constant: Fig. 602.
Nr. 1C-c4 $\text{NaNbO}_3\text{-PbZrO}_3$	1b	Phase diagram: Fig. 603.
	5a	Dielectric constant: Fig. 604a, b.
Nr. 1C-c5 $\text{KNbO}_3\text{-BaTiO}_3$	1b	Phase diagram: Fig. 605. Lattice parameter: Fig. 606.
	5a	Dielectric constant: Fig. 607a, b, c.
Nr. 1C-c6 $\text{KNbO}_3\text{-PbTiO}_3$	1b	Phase diagram: Fig. 608. Lattice parameter: Fig. 609.
	5a	Dielectric constant: Fig. 610a, b.
Nr. 1C-c7 $\text{SrTiO}_3\text{-BiFeO}_3$	1b	Phase diagram: Fig. 611. Lattice parameter: Fig. 612.
	5a	Relaxation phenomena are observed in the range II [65F1].
Nr. 1C-c8 $\text{BaTiO}_3\text{-LaAlO}_3$	1b	Lattice parameter and Curie temperature: Tab. 75.

Tab. 75. BaTiO₃-LaAlO₃. Lattice parameters and Θ_f . [5814]

Concentration mol%		a Å	c Å	c/a	V Å ³	Θ_f °C
BaTiO ₃	LaAlO ₃					
100.0	—	3.9956	4.0352	1.0100	64.42	+120
99.0	1.0	3.9951	4.0345	1.0098	64.39	+ 87
97.5	2.5	3.9949	4.0293	1.0086	64.30	+ 46
95.0	5.0	4.0050	—	1.0000	64.24	— 14
92.5	7.5	4.0011	—	1.0000	64.05	— 85
90.0	10.0	3.9984	—	1.0000	63.92	—133
87.5	12.5	3.9950	—	1.0000	63.76	—
85.0	15.0	3.9906	—	1.0000	63.55	—
75.0	25.0	3.9800	—	1.0000	63.04	—
—	100.0	3.7950	—	1.000	54.65	—

Nr. 1C-c9 BaTiO ₃ -BiFeO ₃	11, 12	Néel temperature and magnetic resonance line width: Fig. 613.
Nr. 1C-c10 PbTiO ₃ -LaAlO ₃	1b, 5a	Phase diagram: Fig. 614. Lattice parameter: Fig. 615. Dielectric constant: Fig. 616.
Nr. 1C-c11 PbTiO ₃ -LaMnO ₃	1b	Transition temperatures: Fig. 617. Lattice parameters: Fig. 618.
Nr. 1C-c12 PbTiO ₃ -LaFeO ₃	1b, 5a	Phase diagram: Fig. 619. Lattice parameter: Fig. 620. Dielectric constant: Fig. 621.
Nr. 1C-c13 PbTiO ₃ -BiFeO ₃	1b, 4, 5a	Phase diagram: Fig. 622a, b. Lattice parameter: Fig. 623a, b. Thermal expansion: Fig. 624. Dielectric constant: Fig. 625.
Nr. 1C-c14 PbZrO ₃ -BiFeO ₃	1b, 5a	Phase diagram: Fig. 626. Lattice parameter: Fig. 627. Dielectric constant: Fig. 628.
Nr. 1C-c15 SrSnO ₃ -BiFeO ₃	1b, 12c	Phase diagram: Fig. 629. Mössbauer absorption: Fig. 630.
Nr. 1C-c16 SrFeO ₃ -BiFeO ₃	1a, 11	Unit cell volume: Fig. 631. Magnetization: Fig. 632.
Nr. 1C-d1 SrTiO ₃ -Sr(Fe _{1/2} Ta _{1/2})O ₃	1b	Phase diagram: Fig. 633.
Nr. 1C-d2 BaTiO ₃ -Ba(Fe _{1/2} Ta _{1/2})O ₃	2b	Phase diagram: Fig. 634.
Nr. 1C-d3 BaTiO ₃ -(K _{1/2} Bi _{1/2})TiO ₃	1b	Curie temperature: Fig. 635. Lattice parameters: Fig. 636.
Nr. 1C-d4 PbTiO ₃ -(Na _{1/2} Bi _{1/2})TiO ₃	1b, 5a	Phase diagram and lattice parameters: Fig. 637. Dielectric constant: Fig. 638.
Nr. 1C-d5 PbTiO ₃ -(K _{1/2} Bi _{1/2})TiO ₃	1b	Curie temperature and lattice parameters: Fig. 639.
Nr. 1C-d6 PbTiO ₃ -(Li _{1/2} La _{1/2})TiO ₃	1b	Curie temperature and lattice parameters: Fig. 640.

Nr. 1C-d7 PbTiO ₃ -(Na _{1/2} La _{1/2})TiO ₃	1b Curie temperature and lattice parameters: Fig. 641.
Nr. 1C-d8 PbTiO ₃ -(Li _{1/2} Ce _{1/2})TiO ₃	1b Lattice parameters: Fig. 642.
Nr. 1C-d9 PbTiO ₃ -(Li _{1/2} Nd _{1/2})TiO ₃	1b Lattice parameters: Fig. 643.
Nr. 1C-d10 PbTiO ₃ -Pb(Mg _{1/2} W _{1/2})O ₃	1b Phase diagram: Fig. 644. Lattice parameters: Fig. 645.
Nr. 1C-d11 PbTiO ₃ -Pb(Fe _{1/2} Ta _{1/2})O ₃	1b Curie temperature: Fig. 646.
Nr. 1C-d12 PbTiO ₃ -Pb(Sc _{1/2} Nb _{1/2})O ₃	1b Curie temperature: Fig. 647.
Nr. 1C-d13 PbTiO ₃ -Pb(Mn _{1/2} Nb _{1/2})O ₃	1b Transition temperature: Fig. 648. Lattice parameters: Fig. 649.
Nr. 1C-d14 PbZrO ₃ -Pb(Sc _{1/2} Nb _{1/2})O ₃	1b Curie temperature: see Fig. 647.
Nr. 1C-d15 PbZrO ₃ -Pb(Fe _{1/2} Ta _{1/2})O ₃	1b Curie temperature: Fig. 650.
Nr. 1C-d16 PbZrO ₃ -(Na _{1/2} Bi _{1/2})ZrO ₃	1b Phase diagram: Fig. 651.
	4 Lattice distortion: Fig. 652.
	5a Dielectric constant: Fig. 653.
Nr. 1C-d17 PbZrO ₃ -(K _{1/2} Bi _{1/2})ZrO ₃	1b Phase diagram: Fig. 654. Lattice parameters: Tab. 76.
	4 Lattice distortion: Fig. 655.
	5a Dielectric constants: Fig. 656.

Tab. 76. (1 - x)PbZrO₃ - x(K_{1/2}Bi_{1/2})ZrO₃. Lattice constants at RT [62B10]

x	a Å	b Å	c Å	
0	5.884	11.768	8.220	orthorhombic
0.10	5.882	11.764	8.227	orthorhombic
0.20	5.877	11.755	8.237	orthorhombic
0.30	5.876	11.751	8.248	orthorhombic
0.40	4.151	—	—	cubic
0.50	4.152	—	—	cubic

Nr. 1C-d18 PbHfO ₃ -Pb(Sc _{1/2} Nb _{1/2})O ₃	1b Curie temperature: see Fig. 647.
Nr. 1C-d19 Pb(Mg _{1/2} W _{1/2})O ₃ -Pb(Mg _{1/2} Nb _{1/2})O ₃	1b Phase diagram: Fig. 657.
Nr. 1C-d20 (Na _{1/2} Bi _{1/2})TiO ₃ -(K _{1/2} Bi _{1/2})TiO ₃	1b Curie temperature: see Fig. 635. Lattice parameters: see Fig. 636.
Nr. 1C-d21 PbZrO ₃ -(Na _{1/2} Bi _{1/2})TiO ₃	1b Phase diagram: Fig. 658. Lattice parameters: Fig. 659.
Nr. 1C-d22 BiFeO ₃ -Sr(Sn _{1/3} Mn _{2/3})O ₃	1b Phase diagram: Fig. 660. Lattice parameters: Fig. 661.
	12c Mössbauer effect: see [65M8]
Nr. 1C-d23 BiFeO ₃ -Pb(Fe _{1/2} Nb _{1/2})O ₃	1b Lattice parameters: Fig. 662.
	5a Dielectric constant: Fig. 663.
	11 Magnetic susceptibility: Fig. 664. Néel temperature and spontaneous magnetization: Fig. 665.

Nr. 1C-e1 $\text{NaNbO}_3\text{-LiNbO}_3$

1b | Phase diagram: Fig. 666.
5a | Dielectric constant: Fig. 667.

Nr. 1C-e2 $\text{NaNbO}_3\text{-NaVO}_3$

5a | Dielectric constant: Fig. 668.
14b | Switching: see Fig. 9.

Nr. 1C-e3 $\text{NaNbO}_3\text{-CaNb}_2\text{O}_6$

1b | Phase diagram: Fig. 669.
5a | Dielectric constant: Fig. 670.

Nr. 1C-e4 $\text{NaNbO}_3\text{-CdNb}_2\text{O}_6$

1b | Phase diagram: Fig. 671, 672.
Lattice parameter: Fig. 673.
5a | Dielectric constant: Fig. 674; Tab. 77.
7a | Piezoelectricity: Fig. 675; Tab. 78.

Tab. 77. $(1-x)\text{NaNbO}_3 - (x/2)\text{CdNb}_2\text{O}_6$ [56L2]. r : capacitance ratio; C : Curie constant; Θ_r , Θ compare Fig. 671, 672

Composition x	Firing conditions			x_{RT}	r	Θ °C	x_{max}	Θ_r °C	C $\cdot 10^4$ °C	Θ_p °C	ρ 10^3 kg m $^{-3}$
	T °C	t hr	atmos- phere								
0.02	1250	1	CdO	230	—	200	2700	375	12	345	3.9
0.05	1250	1	CdO	500	1200	60	4000	375	12	345	4.2
0.10	1250	1	CdO	1000	130	75	4100	320	18	275	4.3
0.15	1250	1	CdO	1400	40	50	8500	285	24	260	4.3
0.20	1250	1	CdO	2300	20	20	10000	250	14	250	4.4
0.25	1250	1	CdO	3500	10	5	15000	220	20	230	4.5
0.30	1220	2	CdO	2700	12	-25	11000	210	20	205	4.6

Tab. 78. $(1-x)\text{NaNbO}_3 - (x/2)\text{CdNb}_2\text{O}_6$ (ceramics) [62K4]

x	0.05	0.10	0.15	0.20	0.25	0.30	
ρ	4.2	4.3	4.3	4.3	4.4	4.2	10^3 kg m $^{-3}$
$f_R \cdot 2r$	3.0	3.0	3.0	3.15	3.36	3.25	10^3 Hz m
s_{11}^E	11.9	11.6	11.6	10.5	9.0	10.1	10^{-12} m 2 N $^{-1}$
$\tan \delta$	0.01	0.01	0.02	0.01	0.01	0.03	
x at Θ_r	4	4.1	8.5	16	13	11	10^3

Nr. 1C-e5 $\text{NaNbO}_3\text{-SrNb}_2\text{O}_6$

1b | Phase diagram: Fig. 676.
Lattice parameter: Fig. 677.
5a | Dielectric constant: Fig. 678.
7a | Electromechanical properties: Fig. 679, 680, 681.

Nr. 1C-e6 $\text{NaNbO}_3\text{-PbNb}_2\text{O}_6$

1b | Phase diagram: Fig. 682.
Lattice parameter: Fig. 683.
7a | Electromechanical properties: Fig. 684.

Nr. 1C-e7 $\text{CdTiO}_3\text{-LiNbO}_3$, $\text{CdTiO}_3\text{-LiTaO}_3$

5a | Dielectric constant: Fig. 685.

Nr. 1C-e8 $\text{SrTiO}_3\text{-Bi}_2\text{O}_3 \cdot 3\text{TiO}_2$

1b | Lattice parameter: Fig. 686.
5a | Dielectric constant: Fig. 687, 688.

Nr. 1C-e9 $\text{BaTiO}_3\text{-BaNb}_2\text{O}_6$

1b | Phase diagram: Fig. 689.

Nr. 1C-e10 BaTiO ₃ -BaTa ₂ O ₆	1b	Lattice parameter: Fig. 690.
	5a	Dielectric constant: Fig. 691.
Nr. 1C-e11 BaTiO ₃ -A ₂ B ₂ O ₇	1b	Curie temperature: Fig. 692.
	5a	Dielectric constant: Fig. 693 ... 697.
Nr. 1C-e12 PbZrO ₃ -PbNb ₂ O ₆		
For the solid solution with PbNb ₂ O ₆ as an end material see 5B-8.		
	1b	Phase diagram: Fig. 698.
	4	Thermal expansion: Fig. 699.
	5	Dielectric constant: Fig. 700.
Nr. 1C-e13 PbZrO ₃ -PbTa ₂ O ₆	1b	Phase diagram: Fig. 701.
	4	Thermal expansion: see Fig. 699.
	5	Dielectric constant: Fig. 702.
Nr. 1C-f1 CaTiO ₃ -SrTiO ₃ -BaTiO ₃	1b	Phase diagram: Fig. 703.
Nr. 1C-f2 CaTiO ₃ -BaTiO ₃ -PbTiO ₃	1b	Phase diagram: Fig. 704, 705. Curie temperature: Fig. 706.
	7a	Electromechanical properties: see Nr. 1A-8, 7a.
Nr. 1C-f3 PbTiO ₃ -PbZrO ₃ -PbO:SnO ₂	1b	Phase diagram: Fig. 707.
	8b	Elastic properties: Fig. 708, 709.
Nr. 1C-f4 PbTiO ₃ -PbHfO ₃ -PbO:SnO ₂	1b	Phase diagram: Fig. 710.
Nr. 1C-f5 PbTiO ₃ -PbZrO ₃ -LaFeO ₃	1b	Phase diagram: Fig. 711. Lattice parameters: Fig. 712.
	1b	Phase diagram: Fig. 713. Lattice parameters: Fig. 714.
Nr. 1C-f7 PbTiO ₃ -PbZrO ₃ -Pb(Mg _{1/3} Nb _{2/3})O ₃	1b	Phase diagram: Fig. 715. Lattice parameters: Fig. 716.
	7a	Electromechanical property: Fig. 717, 718.
Nr. 1C-f8 PbTiO ₃ -PbZrO ₃ -Pb(Fe _{1/2} Nb _{1/2})O ₃	1b	Lattice parameters: Fig. 719. Curie temperature: Fig. 720.
	7a	Electromechanical property: Fig. 721.
Nr. 1C-f9 PbTiO ₃ -PbZrO ₃ -ABO ₃	1b	Phase diagram: Fig. 722.
Nr. 1C-f10 PbTiO ₃ -SrTiO ₃ -LaMnO ₃	1b	Curie temperature: Fig. 723.
Nr. 1C-f11 PbTiO ₃ -LaMnO ₃ -LaMeO ₃ (Me = Fe, Co, Ni, Cr)		
	1b	Transition temperatures: Fig. 724.
	5a	Dielectric constant: Fig. 725.
	11	Magnetic susceptibility: see Fig. 725. Magnetization: Fig. 726.

Nr. 1C-f12 BaTiO ₃ -SrTiO ₃ -LaYO ₃ -LaInO ₃	1b Phase diagram: Fig. 727.
Nr. 1C-f13 CaSnO ₃ -SrSnO ₃ -BaSnO ₃	1b Phase diagram: Fig. 728.
Nr. 1C-f14 (Na-K)(Nb-Ta)O ₃	1b Phase diagram: Fig. 729.
Nr. 1C-f15 (Ca-Ba)(Ti-Zr)O ₃	1b Phase diagram: Fig. 730.
Nr. 1C-f16 (Sr-Pb)(Ti-Zr)O ₃	1b Phase diagram: Fig. 731. Lattice parameter: Fig. 732. Transition temperature: Fig. 733.
	5a Dielectric constant: Fig. 734, 735.
Nr. 1C-f17 (Ba-Pb)(Ti-Zr)O ₃	1b Phase diagram: Fig. 736. Lattice parameter: Fig. 737. Transition temperature: Fig. 738.
	7a Electromechanical properties: Fig. 739, 740.
Nr. 1C-f18 (Ba-Pb)(Ti-Sn)O ₃	1b Phase diagram: Fig. 741, 742. Lattice parameter: Fig. 743. Transition temperature: Fig. 744.
Nr. 1C-f19 BaTiO ₃ -PbTiO ₃ -BaNb ₂ O ₆ -PbNb ₂ O ₆	1b Phase diagram: Fig. 745. Lattice parameter: Fig. 746.

2 WO₃

2A Pure compound

Nr. 2A-1 WO₃, Tungsten trioxide

1a	The anomalous dielectric properties of ceramic specimens of WO ₃ were discovered by OGAWA ^{a)} in 1948. Possibility of ferroelectricity in WO ₃ was pointed out by MATTHIAS ^{b)} in 1949.							a)48N1,48N2 b)49M2 c)49M2 d)60T1 e)60T2 f)52K1 g)56S1
b	phase	VII	VI	V	IV	III	II	I
	state	F ^{a)}						
	crystal system	mono-clinic ^{b)}	tri-clinic ^{b)}	mono-clinic ^{c)}	ortho-rhombic ^{b)}	tetra-gonal ^{d)}	tetra-gonal ^{b)}	tetra-gonal ^{b)}
	space group			P2 ₁ /n ^{c)} -C _{2h} ^{c)}		P4/nmm ^{d)} -D _{2h} ^{d)}		
	θ	-40 ^{b)}	17 ^{b)}	330 ^{a)}	740 ^{a)}	910 ^{a)}	1230 ^{a)}	°C
	T _{melt} = 1473 °C. ρ = 7.157 · 10 ³ kg m ⁻³ at RT. a = 7.30 Å, b = 7.53 Å, c = 7.68 Å, β = 90° 54' at 30 °C. Transparent, bluish green.							21J1 04S1 60T1
2a	Crystal growth: Sublimation method.							51U1, 56T2, 59S3
b	Crystal form: Plate-like.							
3	Crystal structure: Fig. 747, 748; Tab. 79; Fig. 749.							
	phase	VII	VI	V	IV	III	II	I
	Z	4	8	8				
4	Lattice distortion: Tab. 80. Thermal expansion: Fig. 750 ... 754.							60T1
5a	Dielectric constant: κ = 100 ... 300 at liquid air temperature. No reliable dielectric measurements could be carried out at and above room temperature because of high electrical conductivity. dε _{rv-m} /dp = -8.46 · 10 ⁻⁸ °K N ⁻¹ m ² .							49M2
c	Dielectric hysteresis loop was observed at liquid air temperature.							66T4 49M2

* As to the crystal system in the phase VII, possibility of triclinic symmetry was discussed by TANISAKI [60T1].

V Index of substances — Substanzenverzeichnis

This index consists of two parts: part A is for pure compounds (including complex compounds such as $\text{Pb}(\text{Co}_{1/2}\text{Nb}_{1/2})\text{O}_3$ or $\text{Na}_{0.5}\text{Bi}_{1.5}\text{Ti}_4\text{O}_{15}$) and part B is for solid solutions.

V A: In the 1st column the substances are ordered according to the alphabetically arranged gross formula. When their names (e.g. Rochelle salt) and/or their abbreviated names (e.g. TGS) are widely used, they are also included in this column. In the gross formula the numbers of the elements are determined by simple addition.

Compounds containing water of crystallization are, however, listed twice: (1) H and O of the water molecules are included in the gross formula, (2) the water molecules are attached separately to the gross formula. For instance, Rochelle salt is listed in the 1st column as $\text{C}_4\text{H}_4\text{KNaO}_6 \cdot 4\text{H}_2\text{O}$, $\text{C}_4\text{H}_{12}\text{KNaO}_{10}$ and also as Rochelle salt, RS, Seignette salt.

Crystals in which H is replaced by D (e.g. KD_2PO_4) are not listed separately, since data on their properties are presented in the same section as the data on the non-deuterated crystals (e.g. KH_2PO_4).

V B: In the 1st column the gross formula of each end material of a solid solution (e.g. BaTiO_3 or PbTiO_3 for the solid solution $\text{BaTiO}_3\text{--PbTiO}_3$) is listed in the same manner as in the case of pure compounds. Thus the solid solution $\text{BaTiO}_3\text{--PbTiO}_3$ can be found in the 2nd column by looking first for either BaO_3Ti or O_3PbTi in the 1st column of Part B. If the solid solution is expressed by the formula such as $(\text{Sb}_x\text{Bi}_{1-x})\text{SI}$, the end material can be obtained by putting x equal to either 0 or 1. When solid solutions have abbreviated names (e.g. KTN), these are also included in the 1st column.

Since in general one section corresponds to one substance in this volume, the 3rd column gives the section number and the 4th column gives the first page of the section.

Dieses Verzeichnis besteht aus zwei Teilen: Teil A enthält die reinen Verbindungen (einschließlich komplexer Verbindungen wie $\text{Pb}(\text{Co}_{1/2}\text{Nb}_{1/2})\text{O}_3$ oder $\text{Na}_{0.5}\text{Bi}_{1.5}\text{Ti}_4\text{O}_{15}$) und Teil B enthält die Mischkristalle.

V A: In der 1. Spalte sind die Substanzen nach der alphabetisch angeordneten Bruttoformel aufgeführt. Wenn ihre Namen (z. B. Seignette-Salz) und/oder ihre abgekürzten Bezeichnungen (z. B. TGS) häufig gebraucht werden, sind auch sie in dieser Spalte zu finden. In der Bruttoformel ist die Anzahl jedes Elements durch einfache Addition bestimmt.

Verbindungen, die Kristallwasser enthalten, sind zweimal aufgeführt: 1. H und O der Wassermoleküle sind in der Bruttoformel enthalten. 2. die Wassermoleküle werden getrennt der Bruttoformel hinzugefügt (z. B. Seignette-Salz ist in der 1. Spalte aufgeführt als $\text{C}_4\text{H}_4\text{KNaO}_6 \cdot 4\text{H}_2\text{O}$, $\text{C}_4\text{H}_{12}\text{KNaO}_{10}$ und auch als Rochelle-Salz, RS, Seignette-Salz).

Kristalle, in denen H durch D ersetzt ist (z. B. KD_2PO_4), werden nicht gesondert aufgeführt. Daten von ihren Eigenschaften erscheinen in demselben Abschnitt an der gleichen Stelle wie die Daten von den nicht deuterierten Kristallen (z. B. KH_2PO_4).

V B: In der 1. Spalte ist die Bruttoformel jeder Endsubstanz einer Mischkristallreihe (z. B. BaTiO_3 oder PbTiO_3 für die Mischkristallreihe $\text{BaTiO}_3\text{--PbTiO}_3$) in derselben Weise aufgeführt wie im Fall von reinen Verbindungen. So kann die Mischkristallreihe $\text{BaTiO}_3\text{--PbTiO}_3$ in der zweiten Spalte gefunden werden, wenn man zunächst entweder BaO_3Ti oder O_3PbTi in der ersten Spalte von Teil B sucht. Wenn die Mischkristallreihe durch die Formel $(\text{Sb}_x\text{Bi}_{1-x})\text{SI}$ ausgedrückt wird, kann man die Endsubstanz finden, indem man x gleich 0 oder 1 setzt. Wenn Mischkristalle abgekürzte Namen haben (z. B. KTN), sind diese auch in der 1. Spalte enthalten.

Da in diesem Band jeweils ein Abschnitt einer Substanz entspricht, gibt die 3. Spalte die Abschnittsnummer und die 4. Spalte die erste Seite des Abschnitts an.

VA Pure compounds

Gross formula	Chemical formula	Nr.	Page
ADP	$\text{NH}_4\text{H}_2\text{PO}_4$	13A-7	143
$\text{AgC}_2\text{H}_3\text{N}_3\text{O}_5$	$\text{NH}_2\text{CH}_2\text{COOH} \cdot \text{AgNO}_3$	29A-1	191
$\text{Ag}_2\text{H}_3\text{IO}_6$	$\text{Ag}_3\text{H}_3\text{IO}_6$	35-22	209
AgNbO_3	AgNbO_3	35-16	207
AgO_3Ta	AgTaO_3	35-18	207
AgO_3V	AgVO_3	35-20	208
$\text{AlCH}_3\text{NO}_3\text{S}_2 \cdot 12\text{H}_2\text{O}$	$\text{CH}_3\text{NH}_3\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	18A-4	158
$\text{AlCH}_3\text{N}_3\text{O}_8\text{S}_2 \cdot 6\text{H}_2\text{O}$	$\text{C}(\text{NH}_2)_3\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	19A-1	161
$\text{AlCH}_3\text{N}_3\text{O}_{14}\text{S}_2$	$\text{CH}_3\text{NH}_3\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	19A-1	161
$\text{AlCH}_3\text{NO}_3\text{Se}_2 \cdot 12\text{H}_2\text{O}$	$\text{CH}_3\text{NH}_3\text{Al}(\text{SeO}_4)_2 \cdot 12\text{H}_2\text{O}$	18A-4	158
$\text{AlCH}_3\text{N}_3\text{O}_8\text{Se}_2 \cdot 6\text{H}_2\text{O}$	$\text{C}(\text{NH}_2)_3\text{Al}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	18A-10	161
$\text{AlCH}_3\text{N}_3\text{O}_{14}\text{Se}_2$	$\text{C}(\text{NH}_2)_3\text{Al}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	19A-5	166
$\text{AlCH}_3\text{NO}_{20}\text{Se}_2$	$\text{CH}_3\text{NH}_3\text{Al}(\text{SeO}_4)_2 \cdot 12\text{H}_2\text{O}$	19A-5	166
Ammonium metaphosphate		18A-10	161
AsCsH_2O_4	CsH_2AsO_4	35-14	205
AsH_2KO_4	KH_2AsO_4	13A-6	143
		13A-4	141

V Substanzenverzeichnis

Gross formula	Chemical formula	Nr.	Page
AsH ₃ NO ₄	NH ₄ H ₂ AsO ₄	13A-8	147
AsH ₂ O ₄ Rb	RbH ₂ AsO ₄	13A-5	143
Azobenzene	C ₁₂ H ₁₀ N ₂	37-5	216
Azoxybenzene	C ₁₂ H ₁₀ N ₂ O	37-6	216
B ₇ BrCd ₃ O ₁₃	Cd ₃ B ₇ O ₁₃ Br	9A-18	120
B ₇ BrCo ₃ O ₁₃	Co ₃ B ₇ O ₁₃ Br	9A-14	119
B ₇ BrCr ₃ O ₁₃	Cr ₃ B ₇ O ₁₃ Br	9A-11	118
B ₇ BrCu ₃ O ₁₃	Cu ₃ B ₇ O ₁₃ Br	9A-16	119
B ₇ BrFe ₃ O ₁₃	Fe ₃ B ₇ O ₁₃ Br	9A-13	119
B ₇ BrMg ₃ O ₁₃	Mg ₃ B ₇ O ₁₃ Br	9A-10	118
B ₇ BrMn ₃ O ₁₃	Mn ₃ B ₇ O ₁₃ Br	9A-12	119
B ₇ BrNi ₃ O ₁₃	Ni ₃ B ₇ O ₁₃ Br	9A-15	119
B ₇ BrO ₁₃ Zn ₃	Zn ₃ B ₇ O ₁₃ Br	9A-17	120
B ₆ Ca ₂ H ₁₀ O ₁₅	Ca ₂ B ₆ O ₁₁ · 5H ₂ O	21A-1	173
B ₆ Ca ₂ O ₁₁ · 5H ₂ O	Ca ₂ B ₆ O ₁₁ · 5H ₂ O	21A-1	173
B ₇ Cd ₃ ClO ₁₃	Cd ₃ B ₇ O ₁₃ Cl	9A-9	118
B ₇ Cd ₃ IO ₁₃	Cd ₃ B ₇ O ₁₃ I	9A-25	122
B ₇ ClCo ₃ O ₁₃	Co ₃ B ₇ O ₁₃ Cl	9A-5	117
B ₇ ClCr ₃ O ₁₃	Cr ₃ B ₇ O ₁₃ Cl	9A-2	116
B ₇ ClCu ₃ O ₁₃	Cu ₃ B ₇ O ₁₃ Cl	9A-7	118
B ₇ ClFe ₃ O ₁₃	Fe ₃ B ₇ O ₁₃ Cl	9A-4	117
B ₇ ClMg ₃ O ₁₃	Mg ₃ B ₇ O ₁₃ Cl	9A-1	115
B ₇ ClMn ₃ O ₁₃	Mn ₃ B ₇ O ₁₃ Cl	9A-3	117
B ₇ ClNi ₃ O ₁₃	Ni ₃ B ₇ O ₁₃ Cl	9A-6	117
B ₇ ClO ₁₃ Zn ₃	Zn ₃ B ₇ O ₁₃ Cl	9A-8	118
B ₇ Co ₃ IO ₁₃	Co ₃ B ₇ O ₁₃ I	9A-22	121
B ₇ Cr ₃ IO ₁₃	Cr ₃ B ₇ O ₁₃ I	9A-19	120
B ₇ Fe ₃ IO ₁₃	Fe ₃ B ₇ O ₁₃ I	9A-21	120
B ₇ IMn ₃ O ₁₃	Mn ₃ B ₇ O ₁₃ I	9A-20	120
B ₇ INi ₃ O ₁₃	Ni ₃ B ₇ O ₁₃ I	9A-23	121
B ₇ IO ₁₃ Zn ₃	Zn ₃ B ₇ O ₁₃ I	9A-24	121
Ba ₄ Bi ₂ Fe ₂ Nb ₈ O ₃₀	Ba ₄ Bi ₂ Fe ₂ Nb ₈ O ₃₀	5C-g1	104
BaBi ₂ Nb ₈ O ₉	BaBi ₂ Nb ₈ O ₉	7A-7	109
BaBi ₂ NbO ₁₂ Ti ₂	BaBi ₂ Ti ₂ NbO ₁₂	7A-12	110
BaBi ₂ O ₉ Ta ₂	BaBi ₂ Ta ₂ O ₉	7A-8	109
BaBi ₄ O ₁₅ Ti ₄	BaBi ₄ Ti ₄ O ₁₅	7A-14	111
Ba ₂ Bi ₄ O ₁₈ Ti ₅	Ba ₂ Bi ₄ Ti ₅ O ₁₈	7A-19	112
BaC ₁₈ Ca ₂ H ₃₀ O ₁₂	Ca ₂ Ba(CH ₃ CH ₂ COO) ₆	26A-3	184
Ba ₄ Ce ₂ Nb ₈ Ni ₈ O ₃₀	Ba ₄ Ce ₂ Ni ₈ Nb ₈ O ₃₀	5C-d1	104
Ba ₄ Fe ₂ Gd ₂ Nb ₈ O ₃₀	Ba ₄ Gd ₂ Fe ₂ Nb ₈ O ₃₀	5C-g4	104
Ba ₂ Fe ₃ Nb ₇ Nd ₄ O ₃₀	Ba ₂ Nd ₄ Fe ₃ Nb ₇ O ₃₀	5C-h1	104
Ba ₄ Fe ₂ Nb ₈ Nd ₂ O ₃₀	Ba ₄ Nd ₂ Fe ₂ Nb ₈ O ₃₀	5C-g2	104
Ba ₆ FeNb ₈ O ₃₀	Ba ₆ FeNb ₈ O ₃₀	5C-f1	104
Ba ₂ Fe ₃ Nb ₇ O ₃₀ Sm ₄	Ba ₂ Sm ₄ Fe ₃ Nb ₇ O ₃₀	5C-h2	104
Ba ₄ Fe ₂ Nb ₈ O ₃₀ Sm ₂	Ba ₄ Sm ₂ Fe ₂ Nb ₈ O ₃₀	5C-g3	104
Ba ₂ KNb ₅ O ₁₅	KBa ₂ Nb ₅ O ₁₅	5C-b3	103
Ba ₉ MgNb ₁₄ O ₄₅	Ba ₉ MgNb ₁₄ O ₄₅	5C-e1	104
Ba ₂ NaNb ₅ O ₁₅	NaBa ₂ Nb ₅ O ₁₅	5C-b2	103
Ba ₂ Nb ₈ Nd ₄ Ni ₂ O ₃₀	Ba ₂ Nd ₄ Ni ₂ Nb ₈ O ₃₀	5C-c1	104
Ba ₂ Nb ₈ Ni ₂ O ₃₀ Sm ₄	Ba ₂ Sm ₄ Ni ₂ Nb ₈ O ₃₀	5C-c2	104
Ba ₂ Nb ₅ O ₁₅ Rb	RbBa ₂ Nb ₅ O ₁₅	5C-b5	103
Ba ₆ Nb ₈ O ₃₀ Ti ₂	Ba ₆ Ti ₂ Nb ₈ O ₃₀	5C-j1	104
BaNb _{1.5} O _{5.25} Zr _{0.25}	BaZr _{0.25} Nb _{1.5} O _{5.25}	5C-j3	105
BaO ₆ Ta ₂	BaTa ₂ O ₆	5A-3	98
BaO ₃ Ti	BaTiO ₃	1A-8	51
BaO ₃ Zr	BaZrO ₃	1A-12	61
BeC ₆ F ₄ H ₁₇ N ₅ O ₆	(NH ₂ CH ₂ COOH) ₃ H ₃ BeF ₄	28A-3	190
BeF ₄ H ₃ N ₂	(NH ₄) ₂ BeF ₄	14A-2	154
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Bi ₂ CaNb ₂ O ₉	CaBi ₂ Nb ₂ O ₉	7A-3	107
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Bi ₅ GaO ₁₅ Ti ₃	BiBi ₄ Ti ₃ GaO ₁₅	7A-18	112
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Bi _{4.5} K _{0.5} O ₁₅ Ti ₄	K _{0.5} Bi _{4.5} Ti ₄ O ₁₅	7B-4	114
Bi _{1/2} Na _{1/2} O ₃ Ti	(Na _{1/2} Bi _{1/2})TiO ₃	1B1-ii	64
Bi _{4.5} Na _{0.5} O ₁₅ Ti ₄	Na _{0.5} Bi _{4.5} Ti ₄ O ₁₅	7B-3	114
Bi ₂ Nb ₂ O ₉ Pb	PbBi ₂ Nb ₂ O ₉	7A-9	109
Bi ₂ NbO ₁₂ PbTi ₂	PbBi ₂ Ti ₂ NbO ₁₂	7A-13	110
Bi ₂ Nb ₂ O ₉ Sr	SrBi ₂ Nb ₂ O ₉	7A-5	108
Bi ₃ NbO ₉ Ti	BiBi ₂ TiNbO ₉	7A-1	107
Bi ₂ O ₉ PbTa ₂	PbBi ₂ Ta ₂ O ₉	7A-10	110
Bi ₄ O ₁₅ PbTi ₄	PbBi ₄ Ti ₄ O ₁₅	7A-15	111
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Bi ₂ O ₉ SrTa ₂	SrBi ₂ Ta ₂ O ₉	7A-6	109
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C ₄ Cl ₂ H ₁₀ MnN ₂ O ₆	(NH ₂ CH ₂ COOH) ₂ · MnCl ₂ · 2H ₂ O	31A-1	192
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CCrH ₆ N ₂ O ₈ S ₂ · 6H ₂ O	C(NH ₂) ₃ Cr(SO ₄) ₂ · 6H ₂ O	19A-2	164
CCrH ₂₀ NO ₂₀ S ₂	CH ₃ NH ₂ Cr(SO ₄) ₂ · 12H ₂ O	18A-6	160
CCrH ₁₈ N ₂ O ₁₄ S ₂	C(NH ₂) ₃ Cr(SO ₄) ₂ · 6H ₂ O	19A-2	164
CCrH ₆ N ₂ O ₈ Se ₂ · 6H ₂ O	C(NH ₂) ₃ Cr(SeO ₄) ₂ · 6H ₂ O	19A-6	167
CCrH ₁₈ N ₂ O ₁₄ Se ₂	C(NH ₂) ₃ Cr(SeO ₄) ₂ · 6H ₂ O	19A-6	167
C ₂ CuH ₂ O ₄ · 4H ₂ O	Cu(HCOO) ₂ · 4H ₂ O	25A-1	180
C ₂ CuH ₁₀ O ₃	Cu(HCOO) ₂ · 4H ₂ O	25A-1	180
C ₆ FeH ₆ K ₄ N ₆ O ₃	K ₄ Fe(CN) ₆ · 3H ₂ O	22A-2	174
CFeH ₆ NO ₈ S ₂ · 12H ₂ O	CH ₃ NH ₂ Fe(SO ₄) ₂ · 12H ₂ O	18A-7	160
CFeH ₃₀ NO ₂₀ S ₂	CH ₃ NH ₂ Fe(SO ₄) ₂ · 12H ₂ O	18A-7	160
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CGaH ₆ NO ₈ S ₂ · 12H ₂ O	CH ₃ NH ₂ Ga(SO ₄) ₂ · 12H ₂ O	18A-5	160
CGaH ₆ N ₂ O ₈ S ₂ · 6H ₂ O	C(NH ₂) ₃ Ga(SO ₄) ₂ · 6H ₂ O	19A-3	165
CGaH ₁₈ N ₂ O ₁₄ S ₂	C(NH ₂) ₃ Ga(SO ₄) ₂ · 6H ₂ O	19A-3	165
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CGaH ₁₈ N ₂ O ₁₄ Se ₂	C(NH ₂) ₃ Ga(SeO ₄) ₂ · 6H ₂ O	19A-7	167
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C ₄ H ₁₂ KNaO ₁₀	NaKC ₄ H ₄ O ₆ · 4H ₂ O	33A-1	193
C ₄ H ₈ LiNO ₆ · H ₂ O	LiNH ₄ · C ₄ H ₄ O ₆ · H ₂ O	34A-1	199

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$C_4H_6LiO_7Ti$	$LiTiC_4H_4O_6 \cdot H_2O$	34A-2	199
$C_4H_8NNaO_6 \cdot 4H_2O$	$NaNH_4C_4H_4O_6 \cdot 4H_2O$	33A-2	197
$C_4H_{16}NNaO_{10}$	$NaNH_4C_4H_4O_6 \cdot 4H_2O$	33A-2	197
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$CH_6N_3O_8S_2V \cdot 6H_2O$	$C(NH_2)_3V(SO_4)_2 \cdot 6H_2O$	19A-4	166
$CH_{16}N_3O_{14}S_2V$	$C(NH_2)_3V(SO_4)_2 \cdot 6H_2O$	19A-4	166
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$CoCrH_{29}N_2O_{20}S_2$	$Co(NH_2)_2HCr(SO_4)_2 \cdot 12H_2O$	18A-11	161
Colemanite	$Ca_2B_6O_{11} \cdot 5H_2O$ or $CaB_3O_4(OH)_3 \cdot H_2O$	21A-1	173
$Co_{1/4}Mn_{1/4}Nb_{1/2}O_3Pb$	$Pb(Co_{1/4}Mn_{1/4}Nb_{1/2})O_3$	1B3-xvii	70
$Co_{1/4}Mn_{1/4}O_3PbW_{1/2}$	$Pb(Co_{1/4}Mn_{1/4}W_{1/2})O_3$	1B3-xvii	70
$Co_{1/3}Nb_{2/3}O_3Pb$	$Pb(Co_{1/3}Nb_{2/3})O_3$	1B4-iv	71
$Co_{1/2}Nb_{1/2}O_3Pb$	$Pb(Co_{1/2}Nb_{1/2})O_3$	1B3-iv	68
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$Co_{1/2}O_3PbTa_{1/2}$	$Pb(Co_{1/2}Ta_{1/2})O_3$	1B3-xiii	70
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$FeH_4NO_8S_2 \cdot 12H_2O$	$NH_4Fe(SO_4)_2 \cdot 12H_2O$	18A-1	157
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$Fe_2Nb_7Nd_4O_{30}Pb_2$	$Pb_2Nd_4Fe_3Nb_7O_{30}$	5C-h3	104
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$Fe_{1/2}O_3PbW_{1/2}$	$Pb(Fe_{1/2}W_{1/2})O_3$	1B3-xvi	70
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134	LiNbO ₃	LiNbO ₃	17A-1	157
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Gross formula	Chemical formula	Nr.	Page
MnO ₂	MnO ₂	35-31	212
Mn _{1/2} O ₃ PbRe _{1/2}	Pb(Mn _{1/2} Re _{1/2})O ₃	1B2-v	66
Mn _{1/2} O ₃ PbTa _{1/2}	Pb(Mn _{1/2} Ta _{1/2})O ₃	1B3-xi	69
Mn _{1/2} O ₃ PbW _{1/2}	Pb(Mn _{1/2} W _{1/2})O ₃	1B2-iii	66
Mn _{2/3} O ₃ PbW _{1/3}	Pb(Mn _{2/3} W _{1/3})O ₃	1B5-i	73
MnO ₃ Tm	TmMnO ₃	4A-4	96
MnO ₃ Y	YMnO ₃	4A-1	94
MnO ₃ Yb	YbMnO ₃	4A-5	96
Mo ₃ O ₁₂ Sm ₂	Sm ₂ (MoO ₄) ₃	35-1	200
Mo ₃ O ₁₂ Tb ₂	Tb ₂ (MoO ₄) ₃	35-4	201
NNaO ₃	NaNO ₃	11A-1	128
NO ₃ Rb	RbNO ₃	12A-2	133
NaNbO ₃	NaNbO ₃	1A-1	37
NaO ₃ Ta	NaTaO ₃	1A-3	40
NaO ₃ V	NaVO ₃	35-19	208
Nb _{1/2} Ni _{1/2} O ₃ Pb	Pb(Ni _{1/2} Nb _{1/2})O ₃	1B3-v	68
Nb _{2/3} Ni _{1/3} O ₃ Pb	Pb(Ni _{1/3} Nb _{2/3})O ₃	1B4-v	72
Nb ₂ O ₆ Pb	PbNb ₂ O ₆	5A-1	97
Nb ₂ O ₇ Pb ₂	Pb ₂ Nb ₂ O ₇	6A-2	106
Nb _{1/2} O ₃ PbSc _{1/2}	Pb(Sc _{1/2} Nb _{1/2})O ₃	1B3-i	67
Nb _{1/2} O ₃ PbYb _{1/2}	Pb(Yb _{1/2} Nb _{1/2})O ₃	1B3-vii	68
Nb _{2/3} O ₃ PbZn _{1/3}	Pb(Zn _{1/3} Nb _{2/3})O ₃	1B4-ii	71
Nb ₅ O ₁₅ RbSr ₂	RbSr ₂ Nb ₅ O ₁₅	5C-b4	103
Ni _{1/3} O ₃ PbTa _{2/3}	Pb(Ni _{1/3} Ta _{2/3})O ₃	1B4-viii	73
O ₃ PbSc _{1/2} Ta _{1/2}	Pb(Sc _{1/2} Ta _{1/2})O ₃	1B3-x	69
O ₆ Pb ₄ Si	Pb ₄ SiO ₆	35-26	210
O ₆ PbTa ₂	PbTa ₂ O ₆	5A-4	98
O ₃ PbTa _{1/2} Yb _{1/2}	Pb(Yb _{1/2} Ta _{1/2})O ₃	1B3-xiv	70
O ₃ PbTi	PbTiO ₃	1A-9	59
O ₃ Pb ₂ V ₂	Pb ₂ V ₂ O ₆	35-25	210
O ₃ PbZr	PbZrO ₃	1A-13	61
O ₃ RbTa	RbTaO ₃	35-17	207
O ₃ Sn	SnO ₂	35-32	212
O ₄ SrTa ₂	SrTa ₂ O ₆	5A-2	98
O ₇ Sr ₂ Ta ₂	Sr ₂ Ta ₂ O ₇	6A-3	106
O ₃ SrTi	SrTiO ₃	1A-6	45
O ₃ SrZr	SrZrO ₃	1A-11	61
O ₂ Ti	TiO ₂	35-30	212
O ₃ W	WO ₃	2A-1	88
p-azoxyanisole	C ₁₄ H ₁₄ N ₂ O ₃	37-1	215
p-azoxyphenetole	C ₁₆ H ₁₈ N ₂ O ₃	37-2	215
p-butoxybenzoic acid	C ₁₁ H ₁₄ O ₃	37-3	215
Perovskite	CaTiO ₃	1A-5	44
p-methoxycinnamic acid	C ₁₀ H ₁₀ O ₃	37-4	216
Pyrolusite	MnO ₂	35-31	212
Rochelle salt	NaKC ₄ H ₄ O ₆ · 4H ₂ O	33A-1	193
RS	NaKC ₄ H ₄ O ₆ · 4H ₂ O	33A-1	193
Rutile	TiO ₂	35-30	212
Seignette salt	NaKC ₄ H ₄ O ₆ · 4H ₂ O	33A-1	193
SiV ₃	V ₃ Si	36-4	214
SnTe	SnTe	36-2	213
TGS	(NH ₂ CH ₂ COOH) ₃ H ₂ SO ₄	28A-1	185
Tri-glycine tellurate		28A-4	190

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Gross formula

Chemical formula

		Nr.	Page
ABO ₃	ABO ₃ -PbTiO ₃ -PbZrO ₃	1C-f9	87
Al ₂ BaO ₄	BaAl ₂ O ₄ -BaLi ₂ F ₄	8B-1	115
AlLaO ₃	LaAlO ₃ -BaTiO ₃	1C-c8	83
AlLaO ₃	LaAlO ₃ -BiFeO ₃	1C-b11	83
AlLaO ₃	LaAlO ₃ -PbTiO ₃	1C-c10	84
AsH ₄ NO ₄	NH ₄ H ₂ AsO ₄ -TiH ₂ AsO ₄	13B-3	148
AsH ₂ O ₄ Tl	TiH ₂ AsO ₄ -NH ₄ H ₂ AsO ₄	13B-3	148
AsIS	AsSI-SbSI	10B-1	127
BaBi ₂ Nb ₂ O ₉	(Ba-Pb)Bi ₂ Nb ₂ O ₉	7B-5	114
BaBi ₂ Nb ₂ O ₉	Bi ₂ BaNb ₂ O ₉ -Bi ₂ TiNbO ₉	7B-1	113
BaBi ₂ NbO ₁₂ Ti ₂	Bi ₂ BaTi ₂ NbO ₁₂ -Bi ₄ Ti ₂ O ₁₂	7B-2	113
BaF ₄ Li ₂	BaLi ₂ F ₄ -BaAl ₂ O ₄	8B-1	115
BaFe _{1/2} O ₃ Ta _{1/2}	Ba(Fe _{1/2} Ta _{1/2})O ₃ -BaTiO ₃	1C-d2	84
BaHfO ₃	BaHfO ₃ -BaTiO ₃	1C-a24	77
BaHfO ₃	BaHfO ₃ -PbHfO ₃	1C-a18	76
BaNb ₂ O ₆	BaNb ₂ O ₆ -BaTiO ₃	1C-e9	86
BaNb ₂ O ₆	BaNb ₂ O ₆ -BaZrO ₃	5C-j2	105
BaNb ₂ O ₆	BaNb ₂ O ₆ -CaNb ₂ O ₆	5B-1	99
BaNb ₂ O ₆	BaNb ₂ O ₆ -PbNb ₂ O ₆	5B-5	100
BaNb ₂ O ₆	BaNb ₂ O ₆ -SrNb ₂ O ₆	5B-3	99
BaNb ₂ O ₆	BaNb ₂ O ₆ -BaTiO ₃ -PbTiO ₃ -PbNb ₂ O ₆	1C-f19	88
BaNb ₂ O ₆	(Ba-Pb-Sr)(Nb-Ta) ₂ O ₆	5B-15	102
BaNb ₂ O ₆	(Ba-Pb-Ca)(Nb-Ta) ₂ O ₆	5B-15	102
BaO ₃ Sn	BaZr _{0.25} Nb _{1.5} O _{5.25}	5C-j3	105
BaO ₃ Sn	BaSnO ₃ -BaTiO ₃	1C-a25	77
BaO ₃ Sn	BaSnO ₃ -PbO:SnO ₂	1C-a21	76
BaO ₃ Sn	BaSnO ₃ -PbTiO ₃	1C-b10	83
BaO ₃ Sn	(Ba-Pb)(Sn-Ti)O ₃	1C-f18	88
BaO ₃ Sn	BaSnO ₃ -SrSnO ₃	1C-a20	76
BaO ₃ Ta ₂	BaSnO ₃ -CaSnO ₃ -SrSnO ₃	1C-f13	88
BaO ₃ Ta ₂	BaTa ₂ O ₆ -BaTiO ₃	1C-e10	87
BaO ₃ Ta ₂	(Ba-Pb-Ca)(Ta-Nb) ₂ O ₆	5B-15	102
BaO ₃ Ti	(Ba-Pb-Sr)(Ta-Nb) ₂ O ₆	5B-15	102
BaO ₃ Ti	BaTiO ₃ -Ba(Fe _{1/2} Ta _{1/2})O ₃	1C-d2	84
BaO ₃ Ti	BaTiO ₃ -BaHfO ₃	1C-a24	77
BaO ₃ Ti	BaTiO ₃ -BaNb ₂ O ₆	1C-e9	86
BaO ₃ Ti	BaTiO ₃ -BaSnO ₃	1C-a25	77
BaO ₃ Ti	BaTiO ₃ -BaTa ₂ O ₆	1C-e10	87
BaO ₃ Ti	BaTiO ₃ -BaUO ₃	1C-a26	77
BaO ₃ Ti	BaTiO ₃ -BaZrO ₃	1C-a23	77
BaO ₃ Ti	BaTiO ₃ -BiFeO ₃	1C-c9	84
BaO ₃ Ti	BaTiO ₃ -Bi ₄ Ti ₂ O ₁₂	7B-6	114
BaO ₃ Ti	BaTiO ₃ -CaTiO ₃	1C-a7	74
BaO ₃ Ti	BaTiO ₃ -Co ₂ Nb ₂ O ₇	1C-e11	87
BaO ₃ Ti	BaTiO ₃ -Co ₂ Ta ₂ O ₇	1C-e11	87
BaO ₃ Ti	BaTiO ₃ -(K _{1/2} Bi _{1/2})TiO ₃	1C-d3	84
BaO ₃ Ti	BaTiO ₃ -KNbO ₃	1C-c5	83
BaO ₃ Ti	BaTiO ₃ -LaAlO ₃	1C-c8	83
BaO ₃ Ti	BaTiO ₃ -Mn ₂ Nb ₂ O ₇	1C-e11	87
BaO ₃ Ti	BaTiO ₃ -Mn ₂ Ta ₂ O ₇	1C-e11	87
BaO ₃ Ti	BaTiO ₃ -NaNbO ₃	1C-c2	83
BaO ₃ Ti	BaTiO ₃ -Ni ₂ Nb ₂ O ₇	1C-e11	87
BaO ₃ Ti	BaTiO ₃ -Ni ₂ Ta ₂ O ₇	1C-e11	87
BaO ₃ Ti	BaTiO ₃ -PbO:SnO ₂	1C-e11	87
BaO ₃ Ti	BaTiO ₃ -PbTiO ₃	1C-b4	82
BaO ₃ Ti	BaTiO ₃ -PbZrO ₃	1C-a11	75
BaO ₃ Ti	BaTiO ₃ -SrTiO ₃	1C-b3	82
BaO ₃ Ti	BaTiO ₃ -CaTiO ₃ -PbTiO ₃	1C-a9	75
BaO ₃ Ti	BaTiO ₃ -CaTiO ₃ -SrTiO ₃	1C-f2	87
		1C-f1	87

V Substanzenverzeichnis

Gross formula	Chemical formula	Nr.	Page
BaO ₃ Ti	BaTiO ₃ -LaInO ₃ -LaYO ₃ -SrTiO ₃	1C-f12	88
BaO ₃ Ti	BaTiO ₃ -PbTiO ₃ -BaNb ₂ O ₆ -PbNb ₂ O ₆	1C-f19	88
BaO ₃ Ti	(Ba-Ca)(Ti-Zr)O ₃	1C-f15	88
BaO ₃ Ti	(Ba-Pb)(Ti-Sn)O ₃	1C-f18	88
BaO ₃ Ti	(Ba-Pb)(Ti-Zr)O ₃	1C-f17	88
BaO ₃ U	BaUO ₃ -BaTiO ₃	1C-a26	77
BaO ₃ Zr	BaZrO ₃ -BaNb ₂ O ₆	5C-j2	105
BaO ₃ Zr	BaZrO ₃ -BaTiO ₃	1C-a23	77
BaO ₃ Zr	BaZrO ₃ -CaZrO ₃	1C-a12	76
BaO ₃ Zr	BaZrO ₃ -PbTiO ₃	1C-b9	82
BaO ₃ Zr	BaZrO ₃ -PbZrO ₃	1C-a15	76
BaO ₃ Zr	(Ba-Ca)(Zr-Ti)O ₃	1C-f15	88
BaO ₃ Zr	(Ba-Pb)(Zr-Ti)O ₃	1C-f17	88
BaO ₃ Zr	BaZr _{0.25} Nb _{1.5} O _{5.25}	5C-j3	105
BeF ₄ H ₈ N ₂	(NH ₄) ₂ BeF ₄ -(NH ₄) ₂ SO ₄	14B-1	154
BiFeO ₃	BiFeO ₃ -BaTiO ₃	1C-c9	84
BiFeO ₃	BiFeO ₃ -LaAlO ₃	1C-b11	83
BiFeO ₃	BiFeO ₃ -LaCrO ₃	1C-b12	83
BiFeO ₃	BiFeO ₃ -LaFeO ₃	1C-a33	82
BiFeO ₃	BiFeO ₃ -Pb(Fe _{1/2} Nb _{1/2})O ₃	1C-d23	85
BiFeO ₃	BiFeO ₃ -PbTiO ₃	1C-c13	84
BiFeO ₃	BiFeO ₃ -PbZrO ₃	1C-c14	84
BiFeO ₃	BiFeO ₃ -SrFeO ₃	1C-c16	84
BiFeO ₃	BiFeO ₃ -Sr(Sn _{1/3} Mn _{2/3})O ₃	1C-d22	85
BiFeO ₃	BiFeO ₃ -SrSnO ₃	1C-c15	84
BiFeO ₃	BiFeO ₃ -SrTiO ₃	1C-c7	83
BiFeO ₃	BiFeO ₃ -PbTiO ₃ -PbZrO ₃	1C-f6	87
Bi ₅ GaO ₁₅ Ti ₃	Bi ₅ Ti ₃ GaO ₁₅ -Bi ₄ PbTi ₄ O ₁₅	7B-7	114
BiIS	BiSI-SbSI	10B-5	128
Bi _{1/2} K _{1/2} O ₃ Ti	(K _{1/2} Bi _{1/2})TiO ₃ -BaTiO ₃	1C-d3	84
Bi _{1/2} K _{1/2} O ₃ Ti	(K _{1/2} Bi _{1/2})TiO ₃ -(Na _{1/2} Bi _{1/2})TiO ₃	1C-d20	85
Bi _{1/2} K _{1/2} O ₃ Ti	(K _{1/2} Bi _{1/2})TiO ₃ -PbTiO ₃	1C-d5	84
Bi _{1/2} K _{1/2} O ₃ Zr	(K _{1/2} Bi _{1/2})ZrO ₃ -PbZrO ₃	1C-d17	85
Bi _{1/2} Na _{1/2} O ₃ Ti	(Na _{1/2} Bi _{1/2})TiO ₃ -(K _{1/2} Bi _{1/2})TiO ₃	1C-d20	85
Bi _{1/2} Na _{1/2} O ₃ Ti	(Na _{1/2} Bi _{1/2})TiO ₃ -PbTiO ₃	1C-d4	84
Bi _{1/2} Na _{1/2} O ₃ Ti	(Na _{1/2} Bi _{1/2})TiO ₃ -PbZrO ₃	1C-d21	85
Bi _{1/2} Na _{1/2} O ₃ Zr	(Na _{1/2} Bi _{1/2})ZrO ₃ -PbZrO ₃	1C-d16	85
BiNbO ₆	Bi(Nb-Ti)O ₆ -PbNb ₂ O ₆	5B-14	102
Bi ₂ Nb ₆ O ₁₈	Bi ₂ O ₃ · 3Nb ₂ O ₅ -PbNb ₂ O ₆	5B-13	102
Bi ₂ Nb ₂ O ₅ Pb	Bi ₂ PbNb ₂ O ₅ -Bi ₃ TiNbO ₉	7B-1	113
Bi ₂ Nb ₂ O ₅ Pb	Bi ₂ PbNb ₂ O ₅ -BaBi ₂ Nb ₂ O ₉	7B-5	114
Bi ₃ NbO ₁₂ PbTi ₂	Bi ₃ PbTi ₂ NbO ₁₂ -Bi ₄ Ti ₃ O ₁₂	7B-2	113
Bi ₃ Nb ₂ O ₉ Sr	Bi ₂ SrNb ₂ O ₉ -Bi ₃ TiNbO ₉	7B-1	113
Bi ₃ NbO ₁₂ SrTi ₂	Bi ₃ SrTi ₂ NbO ₁₂ -Bi ₄ Ti ₃ O ₁₂	7B-2	113
Bi ₃ NbO ₉ Ti	Bi ₃ TiNbO ₉ -Bi ₂ BaNb ₂ O ₉	7B-1	113
Bi ₃ NbO ₉ Ti	Bi ₃ TiNbO ₉ -Bi ₂ PbNb ₂ O ₉	7B-1	113
Bi ₃ NbO ₉ Ti	Bi ₃ TiNbO ₉ -Bi ₂ SrNb ₂ O ₉	7B-1	113
Bi ₄ O ₁₅ PbTi ₄	Bi ₄ PbTi ₄ O ₁₅ -Bi ₅ Ti ₃ GaO ₁₅	7B-7	114
BiO ₆ Ti	Bi(Ti-Nb)O ₆ -PbNb ₂ O ₆	5B-14	102
Bi ₂ O ₃ Ti ₃	Bi ₂ O ₃ · 3TiO ₂ -PbNb ₂ O ₆	5B-14	102
Bi ₂ O ₃ Ti ₃	Bi ₂ O ₃ · 3TiO ₂ -SrTiO ₃	1C-e8	86
Bi ₄ O ₁₂ Ti ₃	Bi ₄ Ti ₃ O ₁₂ -BaTiO ₃	7B-6	114
Bi ₄ O ₁₂ Ti ₃	Bi ₄ Ti ₃ O ₁₂ -Bi ₃ BaTi ₂ NbO ₁₂	7B-2	113
Bi ₄ O ₁₂ Ti ₃	Bi ₄ Ti ₃ O ₁₂ -Bi ₃ PbTi ₂ NbO ₁₂	7B-2	113
Bi ₄ O ₁₂ Ti ₃	Bi ₄ Ti ₃ O ₁₂ -Bi ₃ SrTi ₂ NbO ₁₂	7B-2	113
BrSSb	SbSBr-SbSI	10B-3	127
C ₆ FH ₁₇ N ₃ O ₉ P	(NH ₂ CH ₂ COOH) ₃ · H ₂ PO ₃ F-		
C ₆ FeH ₆ K ₄ N ₆ O ₃	(NH ₂ CH ₂ COOH) ₃ · H ₂ SO ₄	28B-2	191
C ₆ FeH ₆ K ₄ N ₆ O ₃	K ₄ Fe(CN) ₆ · 3H ₂ O-(NH ₄) ₄ Fe(CN) ₆ · 3H ₂ O	22B-1	176
C ₆ FeH ₆ K ₄ N ₆ O ₃	K ₄ Fe(CN) ₆ · 3H ₂ O-Rb ₄ Fe(CN) ₆ · 3H ₂ O	22B-2	176
C ₆ FeH ₁₆ N ₁₀ · 3H ₂ O	K ₄ Fe(CN) ₆ · 3H ₂ O-Tl ₄ Fe(CN) ₆ · 3H ₂ O	22B-3	177
C ₆ FeH ₂₂ N ₁₀ O ₃	(NH ₄) ₄ Fe(CN) ₆ · 3H ₂ O-K ₄ Fe(CN) ₆ · 3H ₂ O	22B-1	176
	(NH ₄) ₄ Fe(CN) ₆ · 3H ₂ O-K ₄ Fe(CN) ₆ · 3H ₂ O	22B-1	176

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Gross formula	Chemical formula	Nr.	Page
$C_6FeH_5N_6O_4Rb_4$	$Rb_4Fe(CN)_6 \cdot 3H_2O - K_4Fe(CN)_6 \cdot 3H_2O$	22B-2	176
$C_6FeH_5N_6O_4Ti_4$	$Ti_4Fe(CN)_6 \cdot 3H_2O - K_4Fe(CN)_6 \cdot 3H_2O$	22B-3	177
$C_6FeK_4N_6 \cdot 3H_2O$	$K_4Fe(CN)_6 \cdot 3H_2O - (NH_4)_4Fe(CN)_6 \cdot 3H_2O$	22B-1	176
$C_6FeK_4N_6 \cdot 3H_2O$	$K_4Fe(CN)_6 \cdot 3H_2O - Rb_4Fe(CN)_6 \cdot 3H_2O$	22B-2	176
$C_6FeK_4N_6 \cdot 3H_2O$	$K_4Fe(CN)_6 \cdot 3H_2O - Ti_4Fe(CN)_6 \cdot 3H_2O$	22B-3	177
$C_6FeN_4Rb_4 \cdot 3H_2O$	$Rb_4Fe(CN)_6 \cdot 3H_2O - K_4Fe(CN)_6 \cdot 3H_2O$	22B-2	176
$C_6FeN_4Ti_4 \cdot 3H_2O$	$Ti_4Fe(CN)_6 \cdot 3H_2O - K_4Fe(CN)_6 \cdot 3H_2O$	22B-3	177
$C_4H_4KNaO_6 \cdot 4H_2O$	$NaKC_4H_4O_6 \cdot 4H_2O - NaNH_4C_4H_4O_6 \cdot 4H_2O$	33B-1	198
$C_4H_4KNaO_6 \cdot 4H_2O$	$NaKC_4H_4O_6 \cdot 4H_2O - NaTiC_4H_4O_6 \cdot 4H_2O$	33B-2	198
$C_4H_{12}KNaO_{10}$	$NaKC_4H_4O_6 \cdot 4H_2O - NaNH_4C_4H_4O_6 \cdot 4H_2O$	33B-1	198
$C_4H_{12}KNaO_{10}$	$NaKC_4H_4O_6 \cdot 4H_2O - NaTiC_4H_4O_6 \cdot 4H_2O$	33B-2	198
$C_4H_8NNaO_6 \cdot 4H_2O$	$NaNH_4C_4H_4O_6 \cdot 4H_2O - NaKC_4H_4O_6 \cdot 4H_2O$	33B-1	198
$C_4H_{16}NNaO_{10}$	$NaNH_4C_4H_4O_6 \cdot 4H_2O - NaKC_4H_4O_6 \cdot 4H_2O$	33B-1	198
$C_6H_{17}N_5O_{10}S$	$(NH_4CH_2COOH)_3 \cdot H_2SO_4 - (NH_4CH_2COOH)_3 \cdot H_2PO_3F$	28B-2	191
$C_6H_{17}N_5O_{10}S$	$(NH_4CH_2COOH)_3 \cdot H_2SO_4 - (NH_4CH_2COOH)_3 \cdot H_2SeO_4$	28B-1	191
$C_6H_{17}N_5O_{10}Se$	$(NH_4CH_2COOH)_3 \cdot H_2SeO_4 - (NH_4CH_2COOH)_3 \cdot H_2SO_4$	28B-1	191
$C_4H_4NaO_6Ti \cdot 4H_2O$	$NaTiC_4H_4O_6 \cdot 4H_2O - NaKC_4H_4O_6 \cdot 4H_2O$	33B-2	198
$C_4H_{12}NaO_{10}Ti$	$NaTiC_4H_4O_6 \cdot 4H_2O - NaKC_4H_4O_6 \cdot 4H_2O$	33B-2	198
$CaHfO_3$	$CaHfO_3 - PbHfO_3$	1C-a16	76
$CaNb_2O_6$	$CaNb_2O_6 - BaNb_2O_6$	5B-1	99
$CaNb_2O_6$	$CaNb_2O_6 - NaNbO_3$	1C-e3	86
$CaNb_2O_6$	$CaNb_2O_6 - PbNb_2O_6$	5B-2	99
$CaNb_2O_6$	$(Ca-Ba-Pb)(Nb-Ta)_2O_6$	5B-15	102
$Ca_2Nb_2O_7$	$Ca_2Nb_2O_7 - Cd_2Nb_2O_7$	6B-1	106
CaO_3Sn	$CaSnO_3 - PbTiO_3$	1C-b6	82
CaO_3Sn	$CaSnO_3 - SrSnO_3$	1C-a19	76
CaO_3Sn	$CaSnO_3 - SrSnO_3 - BaSnO_3$	1C-f13	88
CaO_3Ta_2	$(Ca-Ba-Pb)(Ta-Nb)_2O_6$	5B-15	102
$Ca_2O_7Ta_2$	$Ca_2Ta_2O_7 - Sr_2Ta_2O_7$	6B-6	106
CaO_3Ti	$CaTiO_3 - BaTiO_3$	1C-a7	74
CaO_3Ti	$CaTiO_3 - CaZrO_3$	1C-a22	76
CaO_3Ti	$CaTiO_3 - NaNbO_3$	1C-c1	83
CaO_3Ti	$CaTiO_3 - PbTiO_3$	1C-a8	75
CaO_3Ti	$CaTiO_3 - SrTiO_3$	1C-a6	74
CaO_3Ti	$CaTiO_3 - BaTiO_3 - PbTiO_3$	1C-f2	87
CaO_3Ti	$CaTiO_3 - BaTiO_3 - SrTiO_3$	1C-f1	87
CaO_3Ti	$(Ca-Ba)(Ti-Zr)O_3$	1C-f15	88
CaO_3Zr	$CaZrO_3 - BaZrO_3$	1C-a12	76
CaO_3Zr	$CaZrO_3 - CaTiO_3$	1C-a22	76
CaO_3Zr	$CaZrO_3 - PbTiO_3$	1C-b5	82
CaO_3Zr	$CaZrO_3 - PbZrO_3$	1C-a13	76
CaO_3Zr	$(Ca-Ba)(Zr-Ti)O_3$	1C-f15	88
$CdNb_2O_6$	$CdNb_2O_6 - NaNbO_3$	1C-e4	86
$CdNb_2O_6$	$CdNb_2O_6 - PbNb_2O_6$	5B-10	101
$Cd_2Nb_2O_7$	$Cd_2Nb_2O_7 - Ca_2Nb_2O_7$	6B-1	106
$Cd_2Nb_2O_7$	$Cd_2Nb_2O_7 - Cd_2Ta_2O_7$	6B-3	106
$Cd_2Nb_2O_7$	$Cd_2Nb_2O_7 - Mg_2Nb_2O_7$	6B-4	106
$Cd_2Nb_2O_7$	$Cd_2Nb_2O_7 - Pb_2Nb_2O_7$	6B-2	106
$Cd_2O_7Ta_2$	$Cd_2Ta_2O_7 - Cd_2Nb_2O_7$	6B-3	106
CdO_3Ti	$CdTiO_3 - LiNbO_3$	1C-e7	86
CdO_3Ti	$CdTiO_3 - LiTaO_3$	1C-e7	86
$Ce_{1/2}Li_{1/2}O_3Ti$	$(Li_{1/2}Ce_{1/2})TiO_3 - PbTiO_3$	1C-d8	85
$CoLaO_3$	$LaCoO_3 - PbTiO_3 - LaMnO_3$	1C-f11	87
$Co_2Nb_2O_7$	$Co_2Nb_2O_7 - BaTiO_3$	1C-e11	87
$Co_2O_7Ta_2$	$Co_2Ta_2O_7 - BaTiO_3$	1C-e11	87
$CrLaO_3$	$LaCrO_3 - BiFeO_3$	1C-b12	83
$CrLaO_3$	$LaCrO_3 - PbTiO_3 - LaMnO_3$	1C-f11	87
$CsNO_3$	$CsNO_3 - RbNO_3$	12B-4	134
$Eu_2Mo_3O_{12}$	$(Eu-Gd)_2(MoO_4)_3$	35-5	201
$Eu_2Mo_3O_{12}$	$(Eu-Tb)_2(MoO_4)_3$	35-6	201

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Gross formula	Chemical formula	Nr.	Page
FeLaO ₃	LaFeO ₃ -BiFeO ₃	1C-a33	82
FeLaO ₃	LaFeO ₃ -PbTiO ₃	1C-c12	84
FeLaO ₃	LaFeO ₃ -PbTiO ₃ -LaMnO ₃	1C-f11	87
FeLaO ₃	LaFeO ₃ -PbTiO ₃ -PbZrO ₃	1C-f5	87
Fe _{1/2} Nb _{1/2} O ₃ Pb	Pb(Fe _{1/2} Nb _{1/2})O ₃ -BiFeO ₃	1C-d23	85
Fe _{1/2} Nb _{1/2} O ₃ Pb	Pb(Fe _{1/2} Nb _{1/2})O ₃ -PbTiO ₃ -PbZrO ₃	1C-f8	87
Fe _{1/2} O ₃ PbTa _{1/2}	Pb(Fe _{1/2} Ta _{1/2})O ₃ -PbTiO ₃	1C-d11	85
Fe _{1/2} O ₃ PbTa _{1/2}	Pb(Fe _{1/2} Ta _{1/2})O ₃ -PbZrO ₃	1C-d15	85
FeO ₃ Sr	SrFeO ₃ -BiFeO ₃	1C-c16	84
Fe _{1/2} O ₃ SrTa _{1/2}	Sr(Fe _{1/2} Ta _{1/2})O ₃ -SrTiO ₃	1C-d1	84
Gd ₂ Mo ₃ O ₁₂	(Gd-Eu) ₂ (MoO ₄) ₃	35-5	201
Gd ₂ Mo ₃ O ₁₂	(Gd-Nd) ₂ (MoO ₄) ₃	35-8	202
Gd ₂ Mo ₃ O ₁₂	(Gd-Tb) ₂ (MoO ₄) ₃	35-9	202
Gd ₂ Mo ₃ O ₁₂	(Gd-Y) ₂ (MoO ₄) ₃	35-7	202
Gd ₂ Mo ₃ O ₁₂	Gd ₂ ((Mo-W)O ₄) ₃	35-10	202
Gd ₂ O ₁₂ W ₃	Gd ₂ ((W-Mo)O ₄) ₃	35-10	202
GeTe	GeTe-SnTe	36-3	214
H ₂ KO ₄ P	KH ₂ PO ₄ -NH ₄ H ₂ PO ₄	13B-1	148
H ₄ N ₂ O ₃	NH ₄ NO ₃ -KNO ₃	12B-1	134
H ₄ NO ₄ P	NH ₄ H ₂ PO ₄ -KH ₂ PO ₄	13B-1	148
H ₄ NO ₄ P	NH ₄ H ₂ PO ₄ -TiH ₂ PO ₄	13B-2	148
H ₈ N ₂ O ₄ S	(NH ₄) ₂ SO ₄ -(NH ₄) ₂ BeF ₄	14B-1	154
H ₂ O ₄ PTI	TiH ₂ PO ₄ -NH ₄ H ₂ PO ₄	13B-2	148
HfO ₃ Pb	PbHfO ₃ -BaHfO ₃	1C-a18	76
HfO ₃ Pb	PbHfO ₃ -CaHfO ₃	1C-a16	76
HfO ₃ Pb	PbHfO ₃ -Pb(Sc _{1/2} Nb _{1/2})O ₃	1C-d18	85
HfO ₃ Pb	PbHfO ₃ -PbTiO ₃	1C-a29	82
HfO ₃ Pb	PbHfO ₃ -PbZrO ₃	1C-a31	82
HfO ₃ Pb	PbHfO ₃ -SrHfO ₃	1C-a17	76
HfO ₃ Pb	PbHfO ₃ -PbTiO ₃ -PbO:SnO ₂	1C-f4	87
HfO ₃ Sr	SrHfO ₃ -PbHfO ₃	1C-a17	76
IK	KI-KNO ₃	12B-3	134
IOSb	SbOI-SbSI	10B-2	127
ISSb	SbSI-AsSI	10B-1	127
ISSb	SbSI-BiSI	10B-5	128
ISSb	SbSI-SbOI	10B-2	127
ISSb	SbSI-SbSBr	10B-3	127
ISSb	SbSI-SbSeI	10B-4	128
ISbSe	SbSeI-SbSI	10B-4	128
InLaO ₃	LaInO ₃ -BaTiO ₃ -LaYO ₃ -SrTiO ₃	1C-f12	88
KNO ₃	KNO ₃ -KI	12B-3	134
KNO ₃	KNO ₃ -NH ₄ NO ₃	12B-1	134
KNO ₃	KNO ₃ -RbNO ₃	12B-2	134
KNbO ₃	KNbO ₃ -BaTiO ₃	1C-c5	83
KNbO ₃	KNbO ₃ -KTaO ₃	1C-a4	74
KNbO ₃	KNbO ₃ -NaNbO ₃	1C-a1	73
KNbO ₃	KNbO ₃ -PbNb ₂ O ₆	5B-11	101
KNbO ₃	KNbO ₃ -PbTiO ₃	1C-c6	83
KNbO ₃	KNbO ₃ -SrNb ₂ O ₆	5C-b6	103
KNbO ₃	(K-Na)(Nb-Ta)O ₃	1C-f14	88
KNbO ₃	K _{0.6} Li _{0.4} (Nb _{0.3} Ta _{0.7})O ₃	5C-k2	105
KNbO ₃	K(Nb _{0.65} Ta _{0.35})O ₃ (KTN)	1C-a5	74
KO ₃ Sb	KSbO ₃ -NaNbO ₃	1C-b2	82
KO ₃ Ta	KTaO ₃ -KNbO ₃	1C-a4	74
KO ₃ Ta	KTaO ₃ -NaNbO ₃	1C-b1	82
KO ₃ Ta	K(Ta _{0.35} Nb _{0.65})O ₃ (KTN)	1C-a5	74
KO ₃ Ta	(K-Na)(Ta _{0.7} Nb _{0.3})O ₃	1C-f14	88
KO ₃ Ta	K _{0.6} Li _{0.4} (Ta _{0.7} Nb _{0.3})O ₃	5C-k2	105
KTN	K(Ta _{0.35} Nb _{0.65})O ₃	1C-a5	74

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82	LaFeO ₃	LaFeO ₃ -PbTiO ₃	1C-c12	84
84	La _{1/2} Li _{1/2} O ₃ Ti	(Li _{1/2} La _{1/2})TiO ₃ -PbTiO ₃	1C-d6	84
87	LaMnO ₃	LaMnO ₃ -PbTiO ₃	1C-c11	84
87	LaMnO ₃	LaMnO ₃ -LaCoO ₃ -PbTiO ₃	1C-f11	87
85	LaMnO ₃	LaMnO ₃ -LaCrO ₃ -PbTiO ₃	1C-f11	87
87	LaMnO ₃	LaMnO ₃ -LaFeO ₃ -PbTiO ₃	1C-f11	87
85	LaMnO ₃	LaMnO ₃ -LaNiO ₃ -PbTiO ₃	1C-f11	87
85	LaMnO ₃	LaMnO ₃ -PbTiO ₃ -SrTiO ₃	1C-f10	87
84	La _{1/2} Na _{1/2} O ₃ Ti	(Na _{1/2} La _{1/2})TiO ₃ -PbTiO ₃	1C-d7	85
84	La ₂ Nb ₆ O ₁₈	La ₂ O ₃ · 3Nb ₂ O ₅ -PbNb ₂ O ₆	5B-12	101
	LaNiO ₃	LaNiO ₃ -LaMnO ₃ -PbTiO ₃	1C-f11	87
201	LaO ₃ Y	LaYO ₃ -BaTiO ₃ -LaInO ₃ -SrTiO ₃	1C-f12	88
202	LiNbO ₃	LiNbO ₃ -CdTiO ₃	1C-e7	86
202	LiNbO ₃	LiNbO ₃ -LiTaO ₃	3B-1	94
202	LiNbO ₃	LiNbO ₃ -NaNbO ₃	1C-e1	86
202	LiNbO ₃	LiNbO ₃ -PbNb ₂ O ₆	5B-11	101
214	Li _{1/2} Nd _{1/2} O ₃ Ti	Li _{0.4} K _{0.6} (Nb _{0.3} Ta _{0.7})O ₃	5C-k2	105
	LiO ₃ Ta	(Li _{1/2} Nd _{1/2})TiO ₃ -PbTiO ₃	1C-d9	85
148	LiO ₃ Ta	LiTaO ₃ -CdTiO ₃	1C-e7	86
134	LiO ₃ Ta	LiTaO ₃ -LiNbO ₃	3B-1	94
148		Li _{0.4} K _{0.6} (Ta _{0.7} Nb _{0.3})O ₃	5C-k2	105
148	Mg ₂ Nb ₂ O ₇	Mg ₂ Nb ₂ O ₇ -Cd ₂ Nb ₂ O ₇	6B-4	106
154	Mg _{1/3} Nb _{2/3} O ₃ Pb	Pb(Mg _{1/3} Nb _{2/3})O ₃ -Pb(Mg _{1/2} W _{1/2})O ₃	1C-d19	85
148	Mg _{1/3} Nb _{2/3} O ₃ Pb	Pb(Mg _{1/3} Nb _{2/3})O ₃ -PbTiO ₃ -PbZrO ₃	1C-f7	87
76	Mg _{1/2} O ₃ PbW _{1/2}	Pb(Mg _{1/2} W _{1/2})O ₃ -Pb(Mg _{1/3} Nb _{2/3})O ₃	1C-d19	85
76	Mg _{1/2} O ₃ PbW _{1/2}	Pb(Mg _{1/2} W _{1/2})O ₃ -PbTiO ₃	1C-d10	85
85	Mn _{1/2} Nb _{1/2} O ₃ Pb	Pb(Mn _{1/2} Nb _{1/2})O ₃ -PbTiO ₃	1C-d13	85
82	Mn _{2/3} O ₃ Sn _{1/3} Sr	Sr(Sn _{1/3} Mn _{2/3})O ₃ -BiFeO ₃	1C-d22	85
82	Mn ₂ Nb ₂ O ₇	Mn ₂ Nb ₂ O ₇ -BaTiO ₃	1C-e11	87
76	Mn ₂ O ₇ Ta ₂	Mn ₂ Ta ₂ O ₇ -BaTiO ₃	1C-e11	87
87	Mo ₃ Nd ₂ O ₁₂	(Nd-Gd) ₂ (MoO ₄) ₃	35-8	202
76	Mo ₃ O ₁₂ Tb ₂	(Tb-Eu) ₂ (MoO ₄) ₃	35-6	201
	Mo ₃ O ₁₂ Tb ₂	(Tb-Gd) ₂ (MoO ₄) ₃	35-9	202
134	Mo ₃ O ₁₂ Y ₂	(Y-Gd) ₂ (MoO ₄) ₃	35-7	202
127	NO ₃ Rb	RbNO ₃ -CsNO ₃	12B-4	134
127	NO ₃ Rb	RbNO ₃ KNO ₃	12B-2	134
128	NaNbO ₃	NaNbO ₃ -BaTiO ₃	1C-c2	83
127	NaNbO ₃	NaNbO ₃ -CaNb ₂ O ₆	1C-e3	86
127	NaNbO ₃	NaNbO ₃ -CaTiO ₃	1C-c1	83
128	NaNbO ₃	NaNbO ₃ -CdNb ₂ O ₆	1C-e4	86
128	NaNbO ₃	NaNbO ₃ -KNbO ₃	1C-a1	73
88	NaNbO ₃	NaNbO ₃ -KSbO ₃	1C-b2	82
134	NaNbO ₃	NaNbO ₃ -KTaO ₃	1C-b1	82
134	NaNbO ₃	NaNbO ₃ -LiNbO ₃	1C-e1	86
134	NaNbO ₃	NaNbO ₃ -NaVO ₃	1C-e2	86
83	NaNbO ₃	NaNbO ₃ -NaSbO ₃	1C-a3	74
74	NaNbO ₃	NaNbO ₃ -NaTaO ₃	1C-a2	74
73	NaNbO ₃	NaNbO ₃ -PbNb ₂ O ₆	1C-e6	86
101	NaNbO ₃	NaNbO ₃ -PbTiO ₃	5B-11	101
83	NaNbO ₃	NaNbO ₃ -PbZrO ₃	1C-c3	83
103	NaNbO ₃	NaNbO ₃ -SrNb ₂ O ₆	1C-c4	83
88	NaNbO ₃	(Na-K)(Nb-Ta)O ₃	1C-e5	86
105	NaO ₃ Sb	NaSbO ₃ -NaNbO ₃	1C-f14	88
74	NaO ₃ Ta	NaTaO ₃ -NaNbO ₃	1C-a3	74
82	NaO ₃ Ta	(Na-K)(Ta-Nb)O ₃	1C-a2	74
74	NaO ₃ V	NaVO ₃ -NaNbO ₃	1C-f14	88
82	Nb ₂ Ni ₂ O ₇	Ni ₂ Nb ₂ O ₇ -BaTiO ₃	1C-e2	86
74	Nb ₂ O ₆ Pb	PbNb ₂ O ₆ -BaNb ₂ O ₆	1C-e11	87
88	Nb ₂ O ₆ Pb	PbNb ₂ O ₆ -Bi ₂ O ₃ · 3Nb ₂ O ₅	5B-5	100
105	Nb ₂ O ₆ Pb	PbNb ₂ O ₆ -Bi ₂ O ₃ · 3TiO ₂	5B-13	102
74	Nb ₂ O ₆ Pb	PbNb ₂ O ₆ -CaNb ₂ O ₆	5B-14	102
			5B-2	99

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$\text{Nb}_2\text{O}_5\text{Pb}$	$\text{PbNb}_2\text{O}_6\text{-CdNb}_2\text{O}_6$	5B-10	101
$\text{Nb}_2\text{O}_5\text{Pb}$	$\text{PbNb}_2\text{O}_6\text{-KNbO}_3$	5B-11	101
$\text{Nb}_2\text{O}_5\text{Pb}$	$\text{PbNb}_2\text{O}_6\text{-La}_2\text{O}_3 \cdot 3\text{Nb}_2\text{O}_5$	5B-12	101
$\text{Nb}_2\text{O}_5\text{Pb}$	$\text{PbNb}_2\text{O}_6\text{-LiNbO}_3$	5B-11	101
$\text{Nb}_2\text{O}_5\text{Pb}$	$\text{PbNb}_2\text{O}_6\text{-NaNbO}_3$	1C-e6,	86
$\text{Nb}_2\text{O}_5\text{Pb}$		5B-11	101
	$\text{PbNb}_2\text{O}_6\text{-PbO} \cdot \text{SnO}_2$	5B-9	101
$\text{Nb}_2\text{O}_5\text{Pb}$	$\text{PbNb}_2\text{O}_6\text{-PbTa}_2\text{O}_6$	5B-6	101
$\text{Nb}_2\text{O}_5\text{Pb}$	$\text{PbNb}_2\text{O}_6\text{-PbTiO}_3$	5B-7	101
$\text{Nb}_2\text{O}_5\text{Pb}$	$\text{PbNb}_2\text{O}_6\text{-PbZrO}_3$	5B-8,	101
		1C-e12	87
	$\text{PbNb}_2\text{O}_6\text{-RbNbO}_3$	5B-11	101
$\text{Nb}_2\text{O}_5\text{Pb}$	$\text{PbNb}_2\text{O}_6\text{-Sm}_2\text{O}_3 \cdot 3\text{Nb}_2\text{O}_5$	5B-12	101
$\text{Nb}_2\text{O}_5\text{Pb}$	$\text{PbNb}_2\text{O}_6\text{-SrNb}_2\text{O}_6$	5B-4	100
$\text{Nb}_2\text{O}_5\text{Pb}$	$\text{PbNb}_2\text{O}_6\text{-Y}_2\text{O}_3 \cdot 3\text{Nb}_2\text{O}_5$	5B-12	101
$\text{Nb}_2\text{O}_5\text{Pb}$	$\text{PbNb}_2\text{O}_6\text{-Bi(Nb-Ti)O}_3$	5B-14	102
$\text{Nb}_2\text{O}_5\text{Pb}$	$\text{PbNb}_2\text{O}_6\text{-BaNb}_2\text{O}_6\text{-BaTiO}_3\text{-PbTiO}_3$	1C-f19	88
$\text{Nb}_2\text{O}_5\text{Pb}$	$(\text{Pb-Ba-Ca})(\text{Nb-Ta})_2\text{O}_6$	5B-15	102
$\text{Nb}_2\text{O}_5\text{Pb}$	$(\text{Pb-Ba-Sr})(\text{Nb-Ta})_2\text{O}_6$	5B-15	102
$\text{Nb}_2\text{O}_5\text{Pb}$	$\text{Pb}_2\text{Nb}_2\text{O}_7\text{-Cd}_2\text{Nb}_2\text{O}_7$	6B-2	106
$\text{Nb}_2\text{O}_7\text{Pb}_2$	$\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-PbHfO}_3$	1C-d18	85
$\text{Nb}_{1/2}\text{O}_3\text{PbSc}_{1/2}$	$\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-PbTiO}_3$	1C-d12	85
$\text{Nb}_{1/2}\text{O}_3\text{PbSc}_{1/2}$	$\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-PbZrO}_3$	1C-d14	85
$\text{Nb}_{1/2}\text{O}_3\text{PbSc}_{1/2}$	$\text{RbNbO}_3\text{-PbNb}_2\text{O}_6$	5B-11	101
NbO_3Rb	$\text{Sm}_2\text{O}_3 \cdot 3\text{Nb}_2\text{O}_5\text{-PbNb}_2\text{O}_6$	5B-12	101
$\text{Nb}_6\text{O}_{18}\text{Sm}_2$	$\text{SrNb}_2\text{O}_6\text{-BaNb}_2\text{O}_6$	5B-3	99
$\text{Nb}_2\text{O}_5\text{Sr}$	$\text{SrNb}_2\text{O}_6\text{-KNbO}_3$	5C-b6	103
$\text{Nb}_2\text{O}_5\text{Sr}$	$\text{SrNb}_2\text{O}_6\text{-NaNbO}_3$	1C-e5	86
$\text{Nb}_2\text{O}_5\text{Sr}$	$\text{SrNb}_2\text{O}_6\text{-PbNb}_2\text{O}_6$	5B-4	100
$\text{Nb}_2\text{O}_5\text{Sr}$	$(\text{Sr-Ba-Pb})(\text{Nb-Ta})_2\text{O}_6$	5B-15	102
$\text{Nb}_2\text{O}_5\text{Sr}$	$\text{Sr}_2\text{Nb}_2\text{O}_7\text{-Sr}_2\text{Ta}_2\text{O}_7$	6B-5	106
$\text{Nb}_2\text{O}_7\text{Sr}_2$	$\text{Ni}_2\text{Ta}_2\text{O}_7\text{-BaTiO}_3$	1C-e11	87
$\text{Ni}_2\text{O}_7\text{Ta}_2$	$\text{Y}_2\text{O}_3 \cdot 3\text{Nb}_2\text{O}_5\text{-PbNb}_2\text{O}_6$	5B-12	101
$\text{Nb}_2\text{O}_{18}\text{Y}_2$		1C-a21	76
O_3PbSn	$\text{PbO} \cdot \text{SnO}_2\text{-BaSnO}_3$	1C-b4	82
O_3PbSn	$\text{PbO} \cdot \text{SnO}_2\text{-BaTiO}_3$	5B-9	101
O_3PbSn	$\text{PbO} \cdot \text{SnO}_2\text{-PbNb}_2\text{O}_6$	1C-a30	82
O_3PbSn	$\text{PbO} \cdot \text{SnO}_2\text{-PbTiO}_3$	1C-a32	82
O_3PbSn	$\text{PbO} \cdot \text{SnO}_2\text{-PbZrO}_3$	1C-f4	87
O_3PbSn	$\text{PbO} \cdot \text{SnO}_2\text{-PbHfO}_3\text{-PbTiO}_3$	1C-f3	87
O_3PbSn	$\text{PbO} \cdot \text{SnO}_2\text{-PbTiO}_3\text{-PbZrO}_3$	1C-f18	88
O_3PbSn	$(\text{Pb-Ba})(\text{Sn-Ti})\text{O}_3$	5B-6	101
O_6PbTa_2	$\text{PbTa}_2\text{O}_6\text{-PbNb}_2\text{O}_6$	1C-e13	87
O_6PbTa_2	$\text{PbTa}_2\text{O}_6\text{-PbZrO}_3$	5B-16	102
O_6PbTa_2	$\text{PbTa}_2\text{O}_6\text{-SrTa}_2\text{O}_6$	5B-15	102
O_6PbTa_2	$(\text{Pb-Ba-Ca})(\text{Ta-Nb})_2\text{O}_6$	5B-15	102
O_6PbTa_2	$(\text{Pb-Ba-Sr})(\text{Ta-Nb})_2\text{O}_6$	1C-b10	83
O_3PbTi	$\text{PbTiO}_3\text{-BaSnO}_3$	1C-a11	75
O_3PbTi	$\text{PbTiO}_3\text{-BaTiO}_3$	1C-b9	82
O_3PbTi	$\text{PbTiO}_3\text{-BaZrO}_3$	1C-c13	84
O_3PbTi	$\text{PbTiO}_3\text{-BiFeO}_3$	1C-b6	82
O_3PbTi	$\text{PbTiO}_3\text{-CaSnO}_3$	1C-a8	75
O_3PbTi	$\text{PbTiO}_3\text{-CaTiO}_3$	1C-b5	82
O_3PbTi	$\text{PbTiO}_3\text{-CaZrO}_3$	1C-d5	84
O_3PbTi	$\text{PbTiO}_3\text{-(K}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$	1C-c6	83
O_3PbTi	$\text{PbTiO}_3\text{-KNbO}_3$	1C-c10	84
O_3PbTi	$\text{PbTiO}_3\text{-LaAlO}_3$	1C-c12	84
O_3PbTi	$\text{PbTiO}_3\text{-LaFeO}_3$	1C-c11	84
O_3PbTi	$\text{PbTiO}_3\text{-LaMnO}_3$	1C-d8	85
O_3PbTi	$\text{PbTiO}_3\text{-(Li}_{1/2}\text{Ce}_{1/2})\text{TiO}_3$	1C-d6	84
O_3PbTi	$\text{PbTiO}_3\text{-(Li}_{1/2}\text{La}_{1/2})\text{TiO}_3$	1C-d9	85
O_3PbTi	$\text{PbTiO}_3\text{-(Li}_{1/2}\text{Nd}_{1/2})\text{TiO}_3$	1C-d4	84
O_3PbTi	$\text{PbTiO}_3\text{-(Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$	1C-d7	85
O_3PbTi	$\text{PbTiO}_3\text{-(Na}_{1/2}\text{La}_{1/2})\text{TiO}_3$		

V Index of substances

Page	Gross formula	Chemical formula	Nr.	Page
101	O_3PbTi	$PbTiO_3-NaNbO_3$	1C-c3	83
101	O_3PbTi	$PbTiO_3-Pb(Fe_{1/2}Ta_{1/2})O_3$	1C-d11	85
101	O_3PbTi	$PbTiO_3-PbHfO_3$	1C-a29	82
101	O_3PbTi	$PbTiO_3-Pb(Mg_{1/2}W_{1/2})O_3$	1C-d10	85
86	O_3PbTi	$PbTiO_3-Pb(Mn_{1/2}Nb_{1/2})O_3$	1C-d13	85
101	O_3PbTi	$PbTiO_3-PbNb_2O_6$	5B-7	101
101	O_3PbTi	$PbTiO_3-PbO:SnO_2$	1C-a30	82
101	O_3PbTi	$PbTiO_3-Pb(Sc_{1/2}Nb_{1/2})O_3$	1C-d12	85
101	O_3PbTi	$PbTiO_3-PbZrO_3$	1C-a27	77
101	O_3PbTi	$PbTiO_3-SrSnO_3$	1C-b8	82
87	O_3PbTi	$PbTiO_3-SrTiO_3$	1C-a10	75
101	O_3PbTi	$PbTiO_3-SrZrO_3$	1C-b7	82
101	O_3PbTi	$PbTiO_3-ABO_3-PbZrO_3$	1C-f9	87
100	O_3PbTi	$PbTiO_3-BaTiO_3-CaTiO_3$	1C-f2	87
101	O_3PbTi	$PbTiO_3-BiFeO_3-PbZrO_3$	1C-f6	87
102	O_3PbTi	$PbTiO_3-LaCoO_3-LaMnO_3$	1C-f11	87
88	O_3PbTi	$PbTiO_3-LaCrO_3-LaMnO_3$	1C-f11	87
102	O_3PbTi	$PbTiO_3-LaFeO_3-LaMnO_3$	1C-f11	87
102	O_3PbTi	$PbTiO_3-LaFeO_3-PbZrO_3$	1C-f5	87
106	O_3PbTi	$PbTiO_3-LaMnO_3-LaNiO_3$	1C-f11	87
85	O_3PbTi	$PbTiO_3-LaMnO_3-SrTiO_3$	1C-f10	87
85	O_3PbTi	$PbTiO_3-Pb(Fe_{1/2}Nb_{1/2})O_3-PbZrO_3$	1C-f8	87
85	O_3PbTi	$PbTiO_3-PbHfO_3-PbO:SnO_2$	1C-f4	87
101	O_3PbTi	$PbTiO_3-Pb(Mg_{1/3}Nb_{2/3})O_3-PbZrO_3$	1C-f7	87
101	O_3PbTi	$PbTiO_3-PbO:SnO_2-PbZrO_3$	1C-f3	87
99	O_3PbTi	$PbTiO_3-BaTiO_3-BaNb_2O_6-PbNb_2O_6$	1C-f19	88
103	O_3PbTi	$(Pb-Ba)(Ti-Sn)O_3$	1C-f18	88
86	O_3PbTi	$(Pb-Ba)(Ti-Zr)O_3$	1C-f17	88
100	O_3PbTi	$Pb(Ti-Zr)O_3$	1C-a28	78
102	O_3PbTi	$(Pb-Sr)(Ti-Zr)O_3$	1C-f16	88
106	O_3PbZr	$PbZrO_3-BaTiO_3$	1C-b3	82
87	O_3PbZr	$PbZrO_3-BaZrO_3$	1C-a15	76
101	O_3PbZr	$PbZrO_3-BiFeO_3$	1C-c14	84
	O_3PbZr	$PbZrO_3-CaZrO_3$	1C-a13	76
76	O_3PbZr	$PbZrO_3-(K_{1/2}Bi_{1/2})ZrO_3$	1C-d17	85
82	O_3PbZr	$PbZrO_3-(Na_{1/2}Bi_{1/2})TiO_3$	1C-d21	85
101	O_3PbZr	$PbZrO_3-(Na_{1/2}Bi_{1/2})ZrO_3$	1C-d16	85
82	O_3PbZr	$PbZrO_3-NaNbO_3$	1C-c4	83
82	O_3PbZr	$PbZrO_3-Pb(Fe_{1/2}Ta_{1/2})O_3$	1C-d15	85
87	O_3PbZr	$PbZrO_3-PbHfO_3$	1C-a31	82
87	O_3PbZr	$PbZrO_3-PbNb_2O_6$	5B-8,	101
88			1C-e12	87
101	O_3PbZr	$PbZrO_3-PbO:SnO_2$	1C-a32	82
87	O_3PbZr	$PbZrO_3-Pb(Sc_{1/2}Nb_{1/2})O_3$	1C-d14	85
102	O_3PbZr	$PbZrO_3-PbTa_2O_6$	1C-e13	87
102	O_3PbZr	$PbZrO_3-PbTiO_3$	1C-a27	77
102	O_3PbZr	$PbZrO_3-SrZrO_3$	1C-a14	76
83	O_3PbZr	$Pb(Zr-Ti)O_3$ (PZT)	1C-a28	78
75	O_3PbZr	$PbZrO_3-ABO_3-PbTiO_3$	1C-f9	87
82	O_3PbZr	$PbZrO_3-BiFeO_3-PbTiO_3$	1C-f6	87
84	O_3PbZr	$PbZrO_3-LaFeO_3-PbTiO_3$	1C-f5	87
82	O_3PbZr	$PbZrO_3-Pb(Fe_{1/2}Nb_{1/2})O_3-PbTiO_3$	1C-f8	87
75	O_3PbZr	$PbZrO_3-Pb(Mg_{1/3}Nb_{2/3})O_3-PbTiO_3$	1C-f7	87
82	O_3PbZr	$PbZrO_3-PbO:SnO_2-PbTiO_3$	1C-f3	87
84	O_3PbZr	$(Pb-Ba)(Zr-Ti)O_3$	1C-f17	88
83	O_3PbZr	$(Pb-Sr)(Zr-Ti)O_3$	1C-f16	88
84	O_3SnSr	$SrSnO_3-BaSnO_3$	1C-a20	76
84	O_3SnSr	$SrSnO_3-BiFeO_3$	1C-c15	84
84	O_3SnSr	$SrSnO_3-CaSnO_3$	1C-a19	76
85	O_3SnSr	$SrSnO_3-PbTiO_3$	1C-b8	82
84	O_3SnSr	$SrSnO_3-BaSnO_3-CaSnO_3$	1C-f13	88
85	O_6SrTa_2	$SrTa_2O_6-PbTa_2O_6$	5B-16	102
84	O_6SrTa_2	$(Sr-Ba-Pb)(Ta-Nb)_2O_6$	5B-15	102
85	$O_7Sr_2Ta_2$	$Sr_2Ta_2O_7-Ca_2Ta_2O_7$	6B-6	106

V Substanzenverzeichnis

Gross formula	Chemical formula	Nr.	Page
$O_7Sr_2Ta_2$	$Sr_2Ta_2O_7-Sr_2Nb_2O_7$	6B-5	106
O_3SrTi	$SrTiO_3-BaTiO_3$	1C-a9	75
O_3SrTi	$SrTiO_3-BiFeO_3$	1C-c7	83
O_3SrTi	$SrTiO_3-Bi_2O_3 \cdot 3TiO_2$	1C-e8	86
O_3SrTi	$SrTiO_3-CaTiO_3$	1C-a6	74
O_3SrTi	$SrTiO_3-PbTiO_3$	1C-a10	75
O_3SrTi	$SrTiO_3-Sr(Fe_{1/2}Ta_{1/2})O_3$	1C-d1	84
O_3SrTi	$SrTiO_3-BaTiO_3-CaTiO_3$	1C-f1	87
O_3SrTi	$SrTiO_3-LaMnO_3-PbTiO_3$	1C-f10	87
O_3SrTi	$SrTiO_3-BaTiO_3-LaInO_3-LaYO_3$	1C-f12	88
O_3SrTi	$(Sr-Pb)(Ti-Zr)O_3$	1C-f16	88
O_3SrZr	$SrZrO_3-PbTiO_3$	1C-b7	82
O_3SrZr	$SrZrO_3-PbZrO_3$	1C-a14	76
O_3SrZr	$(Sr-Pb)(Zr-Ti)O_3$	1C-f16	88
PZT	$Pb(Zr-Ti)O_3$	1C-a28	78
SnTe	SnTe-GeTe	36-3	214

BRIEF ATTACHMENT Q

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Sir:

In response to the Office Action dated July 28, 2004, please consider the
following:

ATTACHMENT Q

J. C. Beckwith

STRUCTURE AND
PROPERTIES OF
INORGANIC SOLIDS

BY

FRANCIS S. GALASSO
United Aircraft Research Laboratories

ILLUSTRATED BY

W. DARBY



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cell is elongated in the c direction; the lead atoms are displaced vertically downwards in the front and back faces and upwards in the side faces. This arrangement corresponds to placement of the atoms in the following special positions in space group $P4/nmm$:

$$2\text{Pb at } (2c): 0, \frac{1}{2}, z; \frac{1}{2}, \frac{1}{2}, 0, \bar{z} \text{ with } z = 0.2385;$$

$$2\text{O at } (2a): 0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0.$$

In this structure both the lead and oxygen atoms are in fourfold coordination with atoms of the other type. The oxygen atoms are in a tetrahedron of lead atoms, while the lead atoms are at the vertex of a square pyramid with oxygen atoms at the base. In the horizontal oxygen sheets, the atoms are in square planar coordination or roughly cubic packing. This structure is illustrated in Fig. 7.1. Other compounds which adopt this structure are listed in Table 7.1.

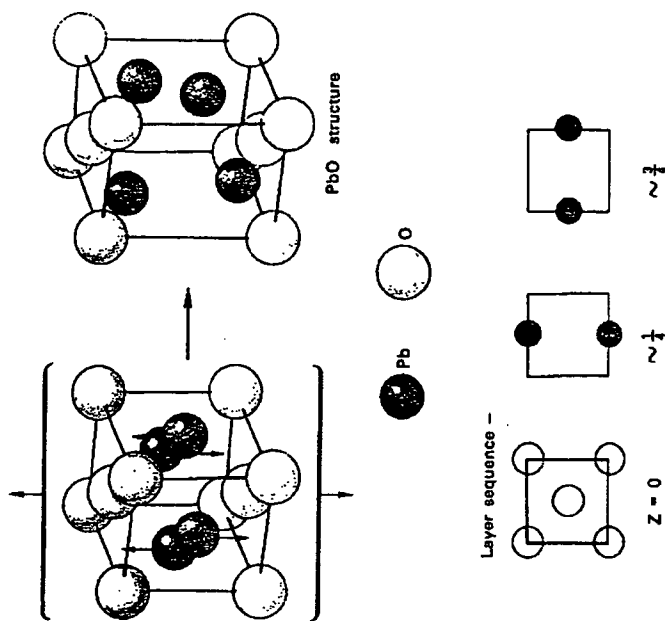


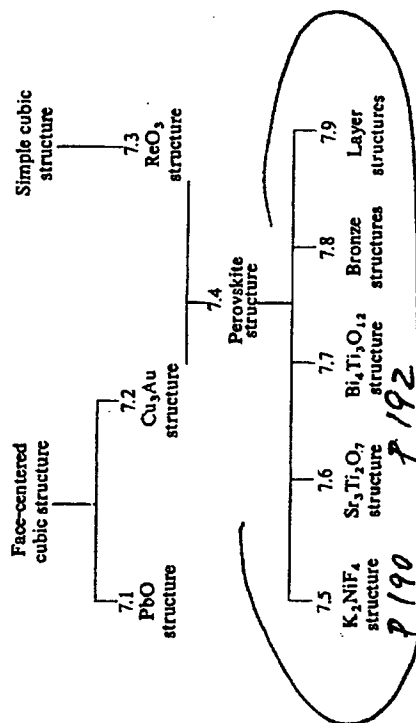
Fig. 7.1 Lead oxide structure

CHAPTER 7

PEROVSKITE TYPE AND RELATED STRUCTURES

THE perovskite-type structures are formed by ABX_3 -type compounds where the A atoms replace some of the X atoms in close-packed cubic layers and the B atoms fit in the octahedrally coordinated sites. In the ordered Cu_3Au structure there are no B atoms; in the ReO_3 structure the A atoms are missing so that there are holes in the close-packed X atom layers. These close-packed layers are perpendicular to the $\langle 111 \rangle$ directions (body diagonals) in the cubic unit cell. Related structures can be built up as close-packed layers of X atoms or by stacking cubic unit cells. The flow diagram showing the relationships between these structures is presented in Table 7.0.

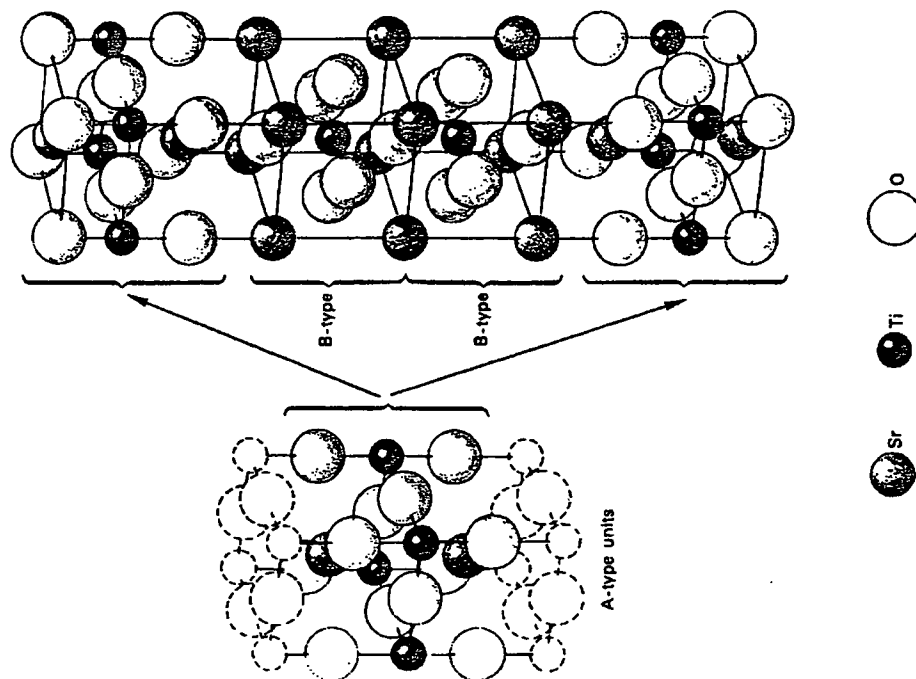
TABLE 7.0.

7.1. Red Lead Oxide, PbO , B10 , $P4/nmm$, Tetragonal

This lead oxide structure can be visualized by starting with an ordered cubic close-packed structure. Lead atoms are placed in the centered positions on the vertical faces of a unit cell and the oxygen atoms in the centered position on the top and bottom faces as well as at the cell corners. The cubic

TABLE 7.5. Phases with the K_2NiF_4 Structure

Phases	Cell size (Å)		Atomic parameters		Refs.
	a_0	c_0	x (A cation)	x (anion)	
Halides, Oxylalides	5.215	16.46			1
	4.074	13.08			2
	4.155	12.74	0.356	0.153	3
	3.977	13.16	0.35	0.15	4
	4.01	13.08	0.352	0.151	5
	3.96	13.67			6
	4.017	13.05			7
	4.084	13.79			8
	4.087	13.71			8
	4.104	13.28			7
	3.84	12.98			9
	4.10	14.1			2
	4.051	14.22			8
	4.296	13.30	0.355	0.155	10
	4.130	13.27	0.355	0.155	10
	3.67	12.08			11
Oxides	4.38	14.79			12
	3.89	11.85			13
	4.34	13.10	0.36	0.145	14
	3.855	12.652	0.360	1.170	15
	3.94	12.15			13
	3.81	12.31			13
	4.345	13.83			12
	3.91	11.93			13
	3.89	12.92	0.347	0.151	16
	3.79	12.43			5
	3.92	12.84			5
	3.85	12.90			17
	3.870	12.74			17
	4.037	12.53	0.353	0.153	10
	3.884	12.60	0.355	0.152	18
Complex Oxides	3.77	12.58			19
	3.75	12.89			19
	3.75	12.5			11
	3.80	12.50			19
	3.85	12.62			19
	3.84	12.52			19
	3.82	12.58			19
	3.86	12.69			19
	3.84	12.71			19
	3.88	12.5			19
	3.80	12.51			19
	3.92	12.78			19

FIG. 7.6 The $SrTi_3O_7$ structure

PEROVSKITE TYPE AND RELATED STRUCTURES

TABLE 7.6. Series of Sr-Ti-O Compounds

Compound	Cell size (Å)		Refs.
	a_0	c_0	
Sr_2TiO_4	3.884	12.60	1
$\text{Sr}_3\text{Ti}_2\text{O}_7$	3.90	20.38	2
$\text{Sr}_4\text{Ti}_3\text{O}_{10}$	3.90	28.1	2
$\text{K}_2\text{Zn}_2\text{F}_7$	4.063	21.22	3

7.7. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ Structure, *Fmm*, Orthorhombic

$\text{Bi}_4\text{Tl}_3\text{O}_{12}$ is one of a series of ferroelectric compounds which can be best described by unit cells of the perovskite structure stacked on one another and separated by bismuth oxygen layers. The structures of $\text{Bi}_2\text{NbO}_5\text{F}$, $\text{Bi}_3\text{NbTiO}_9$, and $\text{BaBi}_4\text{TiO}_{15}$ have been characterized, but in this book only one, $\text{Bi}_4\text{Tl}_3\text{O}_{12}$, will be described. Half the unit cell consists of one and one-half A type perovskite unit cells with an oxygen layer on top and one and one-half B type perovskite unit cells on top of the oxygen layer. The top half of the cell is the mirror image of this one. The unit cell just described is shown in Fig. 7.7a inside the real cell. The actual a and b edges are taken as the face diagonals of the small unit cell of the perovskite structure. The layer sequence is shown in Fig. 7.7b. The atomic positions are given below:

	x	y	z
Bi(1)	(8i)	0	0
(2)	(8i)	0	0.067
Ti(1)	(4b)	0	0.211
(2)	(8i)	0	0.50
O(1)	(8e)	0.25	0.372
(2)	(8f)	0.25	0
(3)	(8i)	0	0.25
(4)	(8i)	0	0.436
(5)	(16j)	0.25	0.308
		0.25	0.128

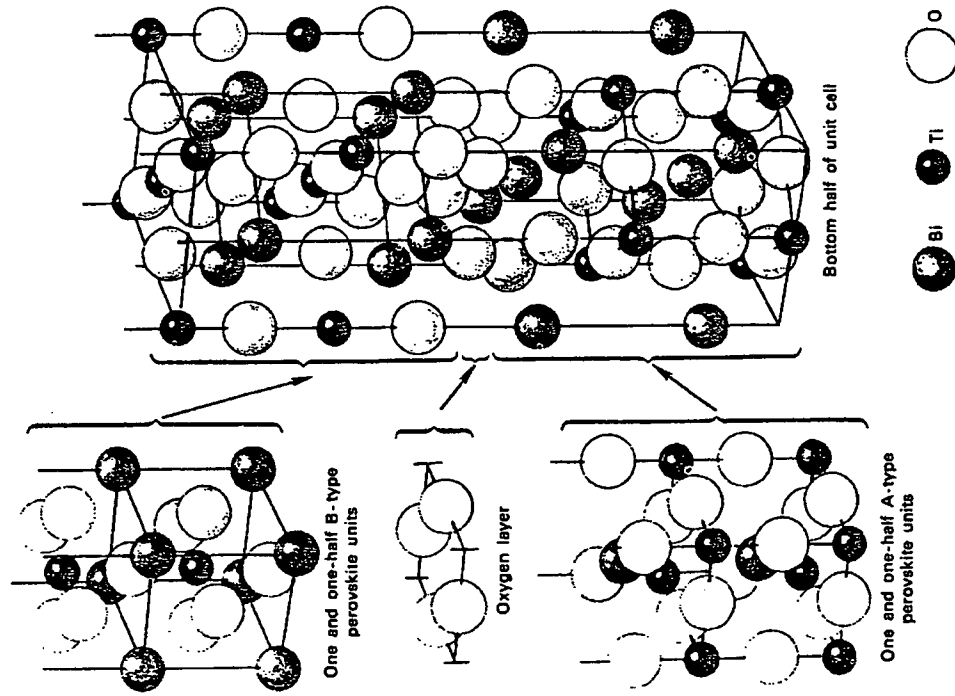
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FIG. 7.7a The $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ structure (one-half the unit cell)

BRIEF ATTACHMENT R

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P.O. Box 1450
Alexandria, VA 22313-1450

FIRST SUPPLEMENTAL AMENDMENT

Sir:

In response to the Office Action dated July 28, 2004, please consider the
following:

ATTACHMENT R

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CRYSTAL STRUCTURES

Second Edition

Ralph W. G. Wyckoff, *University of Arizona, Tucson, Arizona*

VOLUME 4

Miscellaneous Inorganic Compounds, Silicates, and
Basic Structural Information

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Preface

The presentation of data in this volume follows without significant change the pattern established in preceding volumes of this edition. As in Volume V, which was issued earlier, right-hand axes are used in all new drawings.

Since this edition was planned, it has been decided not to enlarge its scope by including intermetallic compounds. Instead, Chapter XIII is devoted to a very abbreviated statement of basic ideas about symmetry and valence. The writer has found that there are many people wishing to use structural data whose training has not prepared them to read with understanding the descriptions of structure now standard. Chapter XIII aims to give this information in as condensed a form as possible. Considering the rapidity with which valence theory is developing, its discussion of valence will undoubtedly seem inadequate to chemists concerned with the subject. In the writer's experience, however, there is little middle ground between a cursory statement such as that given here and a treatment, dealing mostly with organic structures, too long and detailed to be appropriate to the present series.

RALPH W. G. WYCKOFF

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TABLE XI,45

Positions and Parameters of the Atoms in $\text{PbBi}_2\text{Nb}_2\text{O}_8$

Atom	Position	x	y	z
Pb	(4a)	0	0	0.500
Bi	(8c)	0	0.50	0.200
Nb	(8c)	0	0.50	0.422
O(1)	(4a)	0	0	0.00
O(2)	(8b)	$1/4$	$1/4$	0.25
O(3)	(8b)	$1/4$	$1/4$	0.078
O(4)	(8b)	$1/4$	$1/4$	-0.078
O(5)	(8c)	0	0.50	0.156

with the parameters of Table XI,45.

This structure, like those of $\text{Bi}_2\text{Ti}_2\text{O}_{12}$ (IX,f12) and $\text{BaBi}_2\text{Ti}_2\text{O}_{16}$ (XI,13) is built up of alternating Bi_2O_3 and perovskite-like layers.

The following compounds are isostructural:

Crystal	a_0 , Å.	b_0 , Å.	c_0 , Å.
$\text{BaBi}_2\text{Nb}_2\text{O}_8$	5.533	5.533	25.55
$\text{Bi}_2\text{Ta}_2\text{TiO}_8$	5.402	5.436	25.15
$\text{Bi}_2\text{TiNbO}_8$	5.409	5.453	25.16
$\text{CaBi}_2\text{Nb}_2\text{O}_8$	5.435	5.485	24.87
$\text{CaBi}_2\text{Ta}_2\text{O}_8$	5.435	5.498	24.97
$\text{SrBi}_2\text{Nb}_2\text{O}_8$	5.504	5.504	25.06
$\text{SrBi}_2\text{Ta}_2\text{O}_8$	5.509	5.509	25.06
$\text{KBi}_2(\text{Nb}_2\text{O}_8)_2^*$	5.506	5.506	25.26
$\text{NaBi}_2(\text{Nb}_2\text{O}_8)_2^*$	5.47	5.47	26.94

*Two molecules per cell.

At elevated temperatures a_0 approaches b_0 and the symmetry of these compounds becomes tetragonal.

XI,78. The oxychloride mineral *perite*, PbBiO_2Cl , is orthorhombic with a tetramolecular unit of the edge lengths:

$$a_0 = 5.627(50) \text{ Å.}; \quad b_0 = 5.575(20) \text{ Å.}; \quad c_0 = 12.425(90) \text{ Å.}$$

Its space group is V_{17}^{II} ($Bmmb$) with atoms in the positions:

$$\begin{aligned} \text{Pb: } (4c) & \pm (0 \frac{1}{4} u, \frac{1}{4}, u + \frac{1}{2}) & \text{with } u = 0.385 \\ \text{Bi: } (4c) & \text{with } u = 0.090 \\ \text{Cl: } (4c) & \text{with } u = 0.75 \\ \text{O: } (8e) & \pm (u00; u \frac{1}{2} 0; u + \frac{1}{2} 0, \frac{1}{2}; u + \frac{1}{2} \frac{1}{2}, \frac{1}{2}; u + \frac{1}{2} \frac{1}{2}, \frac{1}{2}) \end{aligned}$$

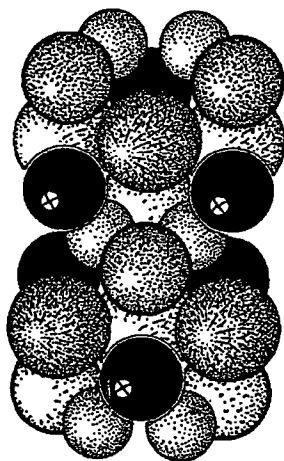
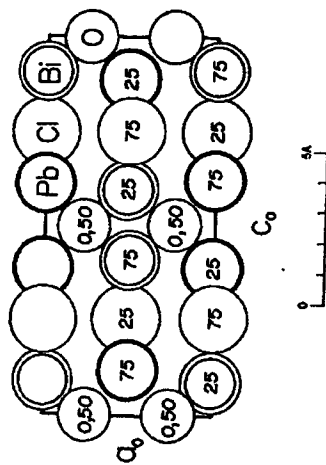


Fig. XI,60a (top). The orthorhombic structure of PbBiO_2Cl projected along its b_0 axis. Fig. XI,60b (bottom). A packing drawing of the orthorhombic PbBiO_2Cl structure seen along its b_0 axis. The lead atoms are black; the bismuth are heavily outlined and hook shaded. The still larger dot-and-line shaded circles are chlorine; atoms of oxygen are smaller and dotted.

The resulting structure is shown in Figure XI,60. Each lead atom has four oxygen neighbors 2.45 Å. away and four more distant chlorine atoms (3.25 and 3.30 Å.). The environment of bismuth is similar, with Bi-O = 2.27 Å. and Bi-Cl = 3.42 and 3.45 Å.

The corresponding antimony compound, which occurs as the mineral *nadorite*, PbSbO_2Cl , is isostructural. For it:

$$a_0 = 5.59 \text{ Å.}; \quad b_0 = 5.43 \text{ Å.}; \quad c_0 = 12.20 \text{ Å.}$$

The atomic positions and parameters are:

$$\begin{aligned} \text{Pb: } (4c) & \text{ with } u = 0.380 \\ \text{Sb: } (4c) & \text{ with } u = 0.078 \\ \text{Cl: } (4c) & \text{ with } u = 0.756 \\ \text{O: } (8e) & \text{ with } u = 0.25 \end{aligned}$$

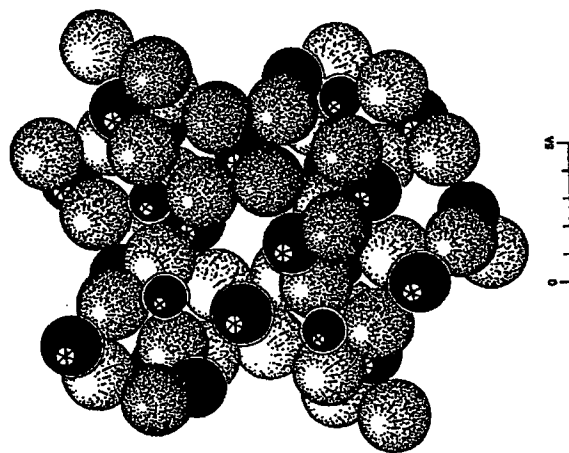
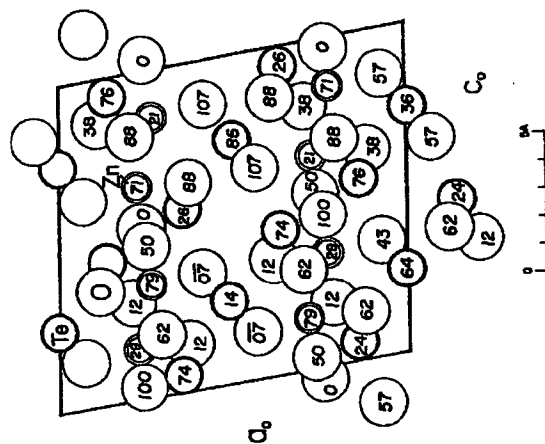


Fig. XI, 90a (top). The monoclinic structure of Zn_7TeO_8 projected along its b_0 axis.
Fig. XI, 90b (bottom). A packing drawing of the monoclinic structure of Zn_7TeO_8 seen along its b_0 axis. The zinc are the small, the tellurium the larger black circles. Atoms

BIBLIOGRAPHY TABLE, CHAPTER XI

Compound	Paragraph	Literature
$\text{Ag}(\text{CN})_3$	2	1966: K&B
$\text{AgCN} \cdot 2\text{AgNO}_3$	1	1965: B&D
$\text{Ag}_2\text{V}_2\text{O}_7$	3	1965: A
$\text{Ag}_2\text{O} \cdot 4\text{B}_2\text{O}_3$	4	1965: KM
$\text{AlBr}_3 \cdot \text{H}_2\text{S}$	6	1956: W,P&W
$\text{Al}_2\text{O}_3\text{C}$	7	1963: J&S
$\text{Al}_2\text{Ta}_2\text{O}_{11}(\text{F},\text{OH})$ (simonite)	9	1962: B&B
$\text{Al}_2\text{B}_4(\text{OH})_2\text{O}_{11}$ (germanjevite)	5	1934: G&K; 1938: S; 1955: G,B&B
$\text{Al}_2\text{C}_2\text{N}_4$	8	1963: J&W; 1966: J&W
$\text{Al}_2\text{C}_2\text{N}_4$	8	1963: J&W
$\text{Al}_2\text{C}_2\text{N}_4$	8	1963: J&W; 1966: J&W
$\text{B}_2\text{S}_2\text{Br}_2$	10	1958: Z
$\text{B}_2\text{H}_4\text{I}_2$	11	1965: H,B&P
BaB_2O_7	12	1965: B&P
$\text{BaBi}_2\text{Nb}_2\text{O}_{10}$	77	1949: A
$\text{BaBi}_2\text{Ti}_2\text{O}_{10}$	13	1950: A
$\text{Ba}_2\text{TiNb}_2\text{O}_{11}$	14	1965: S
$\text{Ba}_2\text{Bi}_2\text{O}_7$	15	1943: A
$\text{Bi}_2\text{Ta}_2\text{TiO}_{10}$	77	1949: A
$\text{Bi}_2\text{TiNbO}_7$	77	1949: A; 1960: I
$\text{Bi}_2\text{RO}_7\text{X}_2$	16	1938: S; 1939: S; 1940: S; 1941: S; S&GH; 1942: S; S&J; 1943: A; 1952: A
$\text{CaB}_2\text{O}_7(\text{OH})$	17	1962: C,C&A
$\text{CaBi}_2\text{Nb}_2\text{O}_{11}$	77	1949: A; 1960: I
$\text{CaBi}_2\text{Ta}_2\text{O}_{11}$	77	1960: I
$\text{Ca}_2\text{Be}_2\text{O}_{11}$	18	1966: H&Y
$\text{Ca}_2\text{Bi}_2\text{O}_7$	15	1943: A
CdBi_2O_7	19	1966: I&KM
$\text{CaBi}_2\text{Be}_2\text{Al}_2\text{O}_{11}$ (rhodizite)	20	1938: S; 1966: B&T
$\text{Ca}_2\text{Re}_2\text{Br}_{11}$	21	1965: E&P; 1966: E&P
$\text{Ca}_2\text{UO}_2\text{Br}_2$	22	1965: M,K&K
$\text{Ca}_2\text{UO}_2\text{Cl}_4$	23	1966: H,R&W
$\text{Ca}_2\text{RhCl}_6 \cdot \text{NH}_4\text{NO}_3$	55	1944: Z&S
$\text{Ca}_2(\text{UO}_2)_2\text{OCl}_4$	24	1964: A&W
$\text{CuCN} \cdot \text{N}_2\text{H}_4$	26	1966: C,L&R
$\text{CuPb}_2\text{Sb}_2\text{S}_4$ (meneghinite)	27	1938: H,P,R&W; 1960: E&H

BRIEF ATTACHMENT S

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

For: **NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION**

Date: March 1, 2005

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

FIRST SUPPLEMENTAL AMENDMENT

Sir:

In response to the Office Action dated July 28, 2004, please consider the
following:

ATTACHMENT S

MODERN OXIDE MATERIALS

Preparation, Properties and Device Applications

Edited by

B. COCKAYNE

Royal Radar Establishment, Malvern, England

and

D. W. JONES

*Centre for Materials Science,
University of Birmingham, England*

1972



ACADEMIC PRESS • London and New York

formed. Both the non-polar high temperature and polar phases can be either orthorhombic and/or tetragonal. It is the single crystal form of the tungsten bronze type ferroelectric compounds which has been primarily studied for both ferroelectric and electro-optic properties.

The first compound of this crystal class reported to be ferroelectric was lead metaniobate, $\text{Pb}_5\text{Nb}_{10}\text{O}_{30}$ (Goodman, 1953), with both orthorhombic a and b axes polar, an exception to the rule for these compounds. Lead metaniobate has a high Curie temperature, 843°K, and was developed as a piezoelectric ceramic for use over a wide temperature range. It is an unusual material with low permittivity, moderate piezoelectric activity and very low mechanical Q. This last point is a serious drawback for many applications but is of considerable use in ultrasonic flow detection where it helps to suppress the phenomenon known as ringing.

A number of solid solutions of lead metaniobate have been studied in the polycrystalline ceramic form but the only one of any practical significance is $(\text{Pb}_{5-x}\text{Ba}_x)\text{Nb}_{10}\text{O}_{30}$. The optimum piezoelectric properties are found near a phase boundary occurring at $x = 2$, which separates two ferroelectric orthorhombic phases. Subbarao (1960) found that for $x < 2$ the polarisation was in the $\langle 110 \rangle$ direction whilst for $x > 2$ the polarisation was parallel to the $\langle 001 \rangle$ direction indicating marked influence of the highly polarisable lead ion on the polar axis. Compositions around the phase boundary possess a relatively low temperature coefficient of the resonance frequency, high mechanical Q and moderately strong piezoelectric activity which renders them suitable for resonant piezoelectric devices requiring frequency stability with temperature.

More complex compounds exhibiting the tungsten bronze structure were reported by Roth and Fang (1960), Ainger et al. (1970) and Isupov (1964). One of the more interesting compounds, barium gadolinium iron niobate, $\text{Ba}_2\text{Gd}_2\text{Fe}_2\text{Nb}_8\text{O}_{30}$, was reported to be a ferroelectric and ferromagnetic ceramic, but investigations with similar ceramics showed that the weak magnetic properties were due to the presence of a second phase, barium hexaferrite.

C. LAYER STRUCTURE OXIDES AND COMPLEX COMPOUNDS

A large number of layer structure compounds of general formula $(\text{Bi}_2\text{O}_5)^{2+}(\text{A}_{x-1}\text{B}_x\text{O}_{3x+1})^{2-}$ have been reported (Smolenskii et al. 1961; Subbarao, 1962), where $\text{A} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}, \text{etc.}$, $\text{B} = \text{Ti}, \text{Nb}, \text{Ta}$ and $x = 2, 3, 4$ or 5 . The structure had been previously investigated by Aurivillius (1949) who described them in terms of alternate $(\text{Bi}_2\text{O}_2)^{2+}$ layers and perovskite layers of oxygen octahedra. Few have been found to be ferroelectric and include $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ($T_c = 583^\circ\text{K}$), $\text{PbBi}_2\text{Ta}_2\text{O}_9$ ($T_c = 703^\circ\text{K}$), $\text{BiBi}_3\text{Ti}_2\text{TiO}_{12}$ or $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($T_c = 948^\circ\text{K}$), $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ ($T_c = 598^\circ\text{K}$) and $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ ($T_c = 583^\circ\text{K}$). Only bismuth titanate $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ has been investigated in detail in the single crystal form and is finding applications in optical stores (Cummins, 1967) because of its unique ferroelectric-optical switching properties. The ceramics of other members have some interest because of their dielectric properties.

More complex compounds and solid solutions are realisable in these layer structure oxides but none have significant practical application.

formed. Both the non-polar high temperature and polar phases can be either orthorhombic and/or tetragonal. It is the single crystal form of the tungsten bronze type ferroelectric compounds which has been primarily studied for both ferroelectric and electro-optic properties.

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More complex compounds and solid solutions are realisable in these layer structure oxides but none have significant practical application.

BRIEF ATTACHMENT T

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

For: **NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION**

Date: March 1, 2005

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

FIRST SUPPLEMENTAL AMENDMENT

Sir:

In response to the Office Action dated July 28, 2004, please consider the
following:

ATTACHMENT T

LANDOLT-BÖRNSTEIN

Numerical Data and Functional Relationships
in Science and Technology

New Series

Editor in Chief: K.-H. Hellwege

Group III: Crystal and Solid State Physics

Volume 3

Ferro- and Antiferroelectric Substances

by Toshio Mitsui and

R. Abe · Y. Furuhashi · K. Gesi · T. Ikeda · K. Kawabe
Y. Makita · M. Marutake · E. Nakamura · S. Nomura
E. Sawaguchi · Y. Shiozaki · I. Tatsuzaki · K. Toyoda

Editors: K.-H. Hellwege and A. M. Hellwege



Springer-Verlag Berlin · Heidelberg · New York 1969

7 Layer-structure oxides

7A Pure compounds of simple type

Nr. 7A-1 $\text{Bi}_2\text{TiNbO}_6$

1a	Dielectric anomaly associated with a phase transition was reported by ISMAILZADE in 1960.		60I1
b	phase	II	I
	state		P ^{a)}
	crystal system	orthorhombic ^{b)}	tetragonal ^{b)}
	space group	Fmm2-C _{2v} ¹⁸	I4/mmm-D _{2h} ¹⁷
	Θ^*	900 ... 950 °C ^{b)}	
	$\rho = 6.4 \cdot 10^3 \text{ kg m}^{-3}$, $a = 5.40 \text{ \AA}$, $b = 5.44 \text{ \AA}$, $c = 25.1 \text{ \AA}$ at RT.		62S17
4	Temperature dependence of lattice parameters: Fig. 868. Linear thermal expansion: Fig. 869.		
5a	Dielectric constant: Fig. 870. $\kappa \approx 100$ at RT. The dielectric constant was not measured in the vicinity of the transition point because of high conductivity. Extrapolation of the Curie temperatures of the solid solution system obtained by the dielectric measurements indicates a transition temperature between 900° and 950 °C for $\text{Bi}_2\text{TiNbO}_6$.		61S11

Nr. 7A-2 $\text{Bi}_2\text{TiTaO}_6$

1a	Phase transition similar to that of $\text{Bi}_2\text{TiNbO}_6$ was reported by SUBBARAO in 1962.		62S17
b	phase	II	I
	state		P
	crystal system	orthorhombic	tetragonal
	space group	Fmm2-C _{2v} ¹⁸	I4/mmm-D _{2h} ¹⁷
	Θ	870 °C	
	$\rho = 8.5 \cdot 10^3 \text{ kg m}^{-3}$, $a = 5.39 \text{ \AA}$, $b/a = 1.007$, $c = 25.1 \text{ \AA}$ at RT.		62S17
4	Linear thermal expansion: see Fig. 869.		
5a	Dielectric constant: $\kappa \approx 140$ at RT.		62S17

Nr. 7A-3 $\text{CaBi}_2\text{Nb}_2\text{O}_9$

1a	Dielectric anomaly associated with a phase transition was discovered by ISMAILZADE in 1960.		60I1
b	phase	II	I
	state		P
	crystal system	orthorhombic	tetragonal
	space group	Fmm2-C _{2v} ¹⁸	I4/mmm-D _{2h} ¹⁷
	Θ	625 °C	
	$\rho = 5.0 \cdot 10^3 \text{ kg m}^{-3}$, $a = 5.39 \text{ \AA}$, $b/a = 1.006$, $c = 25.15 \text{ \AA}$ at RT.		62S17
4	Temperature dependence of lattice parameters: Tab. 104.		
5a	Dielectric constant: Fig. 871. $\kappa \approx 80$ at RT.		62S17

* According to [60I1] Θ is 600 ... 650 °C.

Tab. 104. Temperature dependence of the lattice parameters of $\text{CaBi}_2\text{Nb}_2\text{O}_9$ and $\text{CaBi}_2\text{Ta}_2\text{O}_9$ [60I1]

T	20	100	150	200	250	300	350	400	°C
$\text{CaBi}_2\text{Nb}_2\text{O}_9$									
a	5.442	—	5.453	—	5.458	—	5.465	—	Å
b	5.482 ₈	—	5.484	—	5.487	—	5.491	—	Å
c	24.920	—	24.955	—	24.990	—	25.035	—	Å
b/a	1.0075	—	1.0056	—	1.005 ₃	—	1.0047	—	Å
V	743.5	—	746.0	—	748.5	—	751.0	—	Å ³
$\text{CaBi}_2\text{Ta}_2\text{O}_9$									
a	5.435	5.438	—	5.444	—	5.452	—	5.464	Å
b	5.468 ₈	5.471	—	5.475 ₈	—	5.479	—	5.482 ₈	Å
c	24.970	24.980	—	25.015	—	25.040	—	25.060	Å
b/a	1.006	1.006	—	1.005 ₈	—	1.005	—	1.003 ₈	Å
V	742.0	743.2	—	745.6	—	748.0	—	750.6	Å ³
T	450	500	550	575	600	650	700	°C	
$\text{CaBi}_2\text{Nb}_2\text{O}_9$									
a	5.480	5.485	5.488 ₈	5.495 ₈	—	5.502 ₈	5.504	Å	
b	5.496 ₈	5.501 ₈	5.502 ₈	5.503 ₇	—	5.502 ₈	5.504	Å	
c	25.070	25.080	25.090	25.105	—	25.125	25.140	Å	
b/a	1.0036	1.0029	1.0025	1.0015	—	1.000	1.000	Å	
V	755.0	756.8	758.0	759.3	—	760.7	761.6	Å ³	
$\text{CaBi}_2\text{Ta}_2\text{O}_9$									
a	—	5.470	5.473	—	5.479	5.484	—	Å	
b	—	5.483 ₇	5.484	—	5.479	5.484	—	Å	
c	—	25.070	25.083	—	25.085	25.105	—	Å	
b/a	—	1.002 ₈	1.002 ₄	—	1.000	1.000	—	Å	
V	—	751.9	752.8	—	730.0	755.0	—	Å ³	

Nr. 7A-4 $\text{CaBi}_2\text{Ta}_2\text{O}_9$

1a	Dielectric anomaly associated with a phase transition was discovered by ISMAILZADE in 1960.		60I1
b	phase	II I	60I1
	state	— P	
	crystal system	orthorhombic tetragonal	
	space group	Fmm2-C _{2v} ¹⁸ I4/mmm-D _{2h} ¹⁷	
	θ	575 °C	
	e = 7.5 · 10 ³ kg m ⁻³ .		
	a = 5.428 Å, b/a = 1.006, c = 24.90 Å at RT.		60I1
4	Temperature dependence of lattice parameter: see Tab. 104.		61S11
5a	Dielectric constant: Fig. 872.		

Nr. 7A-5 $\text{SrBi}_2\text{Nb}_2\text{O}_9$

1a	Dielectric anomaly associated with a phase transition was discovered by SMOLENSKII in 1961.			61S11
b	phase	II	I	61S11 *)62S17
	state		P	
	crystal system	orthorhombic	tetragonal	
	θ	420 440*) °C		
	$\rho = 6.9 \cdot 10^3 \text{ kg m}^{-3}$).			
	$a = 5.506 \text{ \AA}$, $b/a = 1.000$, $c = 25.05 \text{ \AA}$ at RT.			
5a	Dielectric constant: Fig. 873. $\kappa \cong 190$ at RT. $\kappa = C/(T - \theta_p)$, where $C = 0.55 \cdot 10^5 \text{ }^\circ\text{C}$, $\theta_p = 390 \text{ }^\circ\text{C}$.			62S15
7a	Piezoelectricity: $d_{33} = 1.0 \cdot 10^{-11} \text{ C N}^{-1}$.			62S17
				62S17

108

Nr. 7A-6 $\text{SrBi}_2\text{Ta}_2\text{O}_9$		
1a	Ferroelectricity in $\text{SrBi}_2\text{Ta}_2\text{O}_9$ was reported by SMOLENSKII in 1961.	61S11
b	phase	II I
	state	F P
	crystal system	orthorhombic tetragonal
	θ	310 °C
	$\rho = 7.5 \cdot 10^3 \text{ kg m}^{-3}$, $a = 5.512 \text{ \AA}$, $b/a = 1.000$, $c = 25.00 \text{ \AA}$ at RT.	61S11 62S15
5a	Dielectric constant: Fig. 874. $\kappa \approx 180$ at RT. $\kappa = C/(T - \theta_p)$, $C = 2.0 \cdot 10^5 \text{ °C}$, $\theta_p = 190 \text{ °C}$.	62S17
c	Spontaneous polarization: $P_s = 5.8 \cdot 10^{-2} \text{ C m}^{-2}$ at 25 °C.	62S17
7a	Piezoelectric constant: $d_{33} = 2.3 \cdot 10^{-11} \text{ C N}^{-1}$.	62S17
Nr. 7A-7 $\text{BaBi}_2\text{Nb}_2\text{O}_9$		
1a	Dielectric anomaly associated with a phase transition was discovered by SMOLENSKII in 1961.	61S11
b	phase	II I
	state	P
	crystal system	orthorhombic tetragonal
	θ	210 °C 200 ^{a)} °C
	$\rho = 6.3 \cdot 10^3 \text{ kg m}^{-3}$, $a = 5.554 \text{ \AA}$, $b/a = 1.000$, $c = 25.60 \text{ \AA}$ at RT.	61S11 ^{a)} 62S17 62S15
5a	Dielectric constant: Fig. 875. $\kappa = 280$ at RT.	62S17
Nr. 7A-8 $\text{BaBi}_2\text{Ta}_2\text{O}_9$		
1a	Dielectric anomaly associated with a phase transition was discovered by SMOLENSKII in 1961.	61S11
b	phase	II I
	state	P
	crystal system	orthorhombic tetragonal
	θ	110 ^{a)} °C
	According to [61S11] θ is 70 °C. $\rho = 8.4 \cdot 10^3 \text{ kg m}^{-3}$, $a = 5.556 \text{ \AA}$, $b/a = 1.000$, $c = 25.50 \text{ \AA}$ at RT.	61S11 ^{a)} 62S17 61S11 62S15
5a	Dielectric constant: Fig. 876. $\kappa = 400$ at RT.	62S17
Nr. 7A-9 $\text{PbBi}_2\text{Nb}_2\text{O}_9$		
1a	Dielectric anomaly associated with a phase transition in $\text{PbBi}_2\text{Nb}_2\text{O}_9$ was reported by SMOLENSKII in 1959.	59S8
b	phase	II I
	state	P
	crystal system	orthorhombic tetragonal
	θ	526 °C 550 ^{a)} °C
	$\rho = 7.6 \cdot 10^3 \text{ kg m}^{-3}$, $a = 5.488 \text{ \AA}$, $b/a = 1.002$, $c = 25.55 \text{ \AA}$ at RT.	59S8 ^{a)} 61S15 62S15
3	Crystal structure: Fig. 877.	
4	Temperature dependence of lattice parameters: Fig. 878.	
5a	Dielectric constant: Fig. 879. $\kappa = 170$ at RT. $\kappa = C/(T - \theta_p)$, $C = 1.3 \cdot 10^5 \text{ °K}$, $\theta_p = 510 \text{ °C}$.	62S17
7a	Piezoelectric constant: $d_{33} = 1.5 \cdot 10^{-11} \text{ C N}^{-1}$.	62S17

Nr. 7A-10 $\text{PbBi}_2\text{Ta}_2\text{O}_9$

1a	Ferroelectricity was reported by SUBBARAO ^{a)} and SMOLENSKII ^{b)} independently in 1961.			^{a)} 61S15 ^{b)} 61S11
b	phase	II	I	
	state	F	P	
	crystal system	orthorhombic	tetragonal	
	θ	430 °C		61S15 61S11
	$\rho = 9.0 \cdot 10^3 \text{ kg m}^{-3}$ $a = 5.496 \text{ \AA}$, $b/a = 1.000$, $c = 25.40 \text{ \AA}$ at RT.			62S15
5a	Dielectric constant: Fig. 880. $\kappa = 180$ at RT. $\kappa = C/(T - \theta_p)$, $C = 3.7 \cdot 10^4 \text{ °C}$, $\theta_p = 325 \text{ °C}$.			62S17
7a	Piezoelectric constant: $d_{33} = 5 \cdot 10^{-13} \text{ C N}^{-1}$.			62S17

Nr. 7A-11 $\text{Bi}_4\text{Ti}_3\text{O}_{13}$

1a	Ferroelectricity in $\text{Bi}_4\text{Ti}_3\text{O}_{13}$ was reported by VAN UITERT et al. in 1961.			61V2
b	phase	II	I	
	state	F	P	
	crystal system	monoclinic ^{a)} (pseudo-orthorhombic)	tetragonal	61V2 ^{a)} 67C6
	θ	675 °C		
	Unit cell is very nearly orthorhombic with the lattice parameters: $a_{\text{orth}} = 5.411 \text{ \AA}$, $b_{\text{orth}} = 5.448 \text{ \AA}$, $c_{\text{orth}} = 32.85 \text{ \AA}$ at RT. Relations between crystallographic axes: Fig. 881. P_s lies in a direction tilted at approximately 7° (or less) from the major crystal surface in a plane parallel to the pseudo-orthorhombic $b - c$ plane.			
2a	Crystal growth: Cooling method from melt consisting of 100 Bi_2O_3 and 5 TiO_2 (weight ratio).			67C6
3	Crystal structure: Fig. 882.			61V2
4	Temperature dependence of lattice parameter: Fig. 883. Thermal expansion: Fig. 884.			
5a	Dielectric constant: Fig. 885.			
c	P_s and E_c : Fig. 886, 887. TAMBOVISEV et al. measured P_s and E_c by applying a field parallel to the c_{orth} direction, $P_s = 1.99 \cdot 10^{-3} \text{ C m}^{-2}$, $E_c = 1.13 \cdot 10^4 \text{ V m}^{-1}$. According to [67C6], the spontaneous polarization lies in the pseudo-orthorhombic (100) plane and has a value larger than $30 \cdot 10^{-3} \text{ C m}^{-2}$.			63T1 67C6
	Piezoelectric constant: $d_{33} = 2.0 \cdot 10^{-11} \text{ C N}^{-1}$.			
10	Conductivity: see			61S17
14a	Domain structure: see Domains have been observed by polarized light.			64P3
b	Switching: Fig. 888, 889. See also Fig. 892, Tab. 105 and:			64P3 66C7
	Twining structure: see			66P6
17				64P3

Nr. 7A-12 $\text{BaBi}_2\text{Ti}_2\text{NbO}_{12}$

1a	Dielectric anomaly associated with a phase transition was reported by SUBBARAO in 1961.			61S15
b	phase	II	I	
	state		P	
	crystal system	pseudo-tetragonal	tetragonal	
	θ	270 °C		61S15
	$a = 3.874 \text{ \AA}$, $c = 33.70 \text{ \AA}$ at RT.			

Nr. 7A-13 $\text{PbBi}_2\text{Ti}_2\text{NbO}_{12}$

1a	Dielectric anomaly associated with a phase transition was reported by SUBBARAO in 1961.			61S15
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* Point group is m.

* Point group is m.

1b	phase	II	I	
	state		P	
	crystal system	pseudo-tetragonal	tetragonal	
	Θ	290 °C		61S15
	$a = 3.687 \text{ \AA}, c = 33.55 \text{ \AA}$ at RT.			61S15

Nr. 7A-14 BaBi₄Ti₄O₁₅

1a	Dielectric anomaly associated with a phase transition was reported independently by SUBBARAO ^{a)} and by SMOLENSKII ^{b)} in 1961. Ferroelectric activity was reported independently by FANG et al. in 1961 ^{c)} .			^{a)} 61S15 ^{b)} 61S11 ^{c)} 61F7
b	phase	II	I	
	state	F	P	61F7
	crystal system	orthorhombic (or pseudo-orthorhombic)	tetragonal	
	Θ	375 °C 395 ^{a)} °C		^{a)} 61S15
	$\rho = 5.7 \cdot 10^3 \text{ kg m}^{-3}$ $a = 5.461 \text{ \AA}, b/a = 1.000, c = 41.85 \text{ \AA}$ at RT.			62S15
3	Crystal structure: Fig. 890.			
5a	Dielectric constant: Fig. 891. $\kappa = 150$ at RT. $\kappa = C/(T - \Theta_p)$, $C = 2.5 \cdot 10^5 \text{ °K}$, $\Theta_p = 335 \text{ °C}$.			61S15
7a	Piezoelectric constant: $d_{33} = 2.3 \cdot 10^{-11} \text{ C N}^{-1}$.			62S17
14b	Switching: Fig. 892; Tab. 105.			

Tab. 105. BaBi₄Ti₄O₁₅, Ba₂Bi₄Ti₄O₁₅, Bi₄Ti₄O₁₅, BaTiO₃ (for comparison). Switching parameters in comparison with those of BaTiO₃ [62F7]. $t_s = t_{\infty} \exp(+\alpha/E)$, t_s = switching time

	BaTiO ₃	Bi ₄ Ti ₄ O ₁₅	BaBi ₄ Ti ₄ O ₁₅	Ba ₂ Bi ₄ Ti ₄ O ₁₅	
α	6.1	41	23	76	10^4 V m^{-1}
t_{∞}	0.4	10^{-2}	1.5	10^{-2}	$\mu \text{ sec}$

Nr. 7A-15 PbBi₄Ti₄O₁₅

1a	Dielectric anomaly associated with a phase transition was reported by SUBBARAO in 1961.			61S15
b	phase	II	I	
	state		P	
	crystal system	orthorhombic (possibly)	tetragonal	61S15
	Θ	570 °C		
	$\rho = 6.6 \cdot 10^{-3} \text{ kg m}^{-3}$ $a = 5.437 \text{ \AA}, b/a = 1.000, c = 41.35 \text{ \AA}$ at RT.			62S15
5a	Dielectric constant: Fig. 893. $\kappa = 220$ at RT. $\kappa = C/(T - \Theta_p)$, $C = 1.4 \cdot 10^5 \text{ °C}$, $\Theta_p = 552 \text{ °C}$.			61S15 62S17
7a	Piezoelectric constant: $d_{33} = 2.3 \cdot 10^{-11} \text{ C N}^{-1}$.			62S17

Nr. 7A-16 SrBi₄Ti₄O₁₅

1a	Dielectric anomaly associated with a phase transition was reported by SUBBARAO in 1961.			61S15
b	phase	II	I	
	state		P	
	crystal system	orthorhombic (possibly)	tetragonal	61S15
	Θ	530 °C		
	$\rho = 5.2 \cdot 10^3 \text{ kg m}^{-3}$ $a = 5.428 \text{ \AA}, b/a = 1.000, c = 40.95 \text{ \AA}$ at RT.			62S17 62S15
5a	Dielectric constant: Fig. 894. $\kappa = 190$ at RT. $\kappa = C/(T - \Theta_p)$, $C = 0.68 \cdot 10^5 \text{ °C}$, $\Theta_p = 485 \text{ °C}$.			62S17
7a	Piezoelectric constant: $d_{33} = 1.5 \cdot 10^{-12} \text{ C N}^{-1}$.			62S17

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Nr. 7A-17 $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$

1a	$\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ was investigated by SUBBARAO in 1962. No dielectric anomaly has been detected.	62S17
b	Orthorhombic: $a = 5.418 \text{ \AA}$, $b/a = 1.002$, $c = 40.75 \text{ \AA}$ at RT. $\rho = 4.7 \cdot 10^3 \text{ kg m}^{-3}$.	62S15
5a	Dielectric constant: Fig. 895. $\kappa = 120$ at RT.	61S11

Nr. 7A-18 $\text{Bi}_5\text{Ti}_3\text{GaO}_{15}$

1a	$\text{Bi}_5\text{Ti}_3\text{GaO}_{15}$ was investigated by SUBBARAO in 1962. No dielectric anomaly has been detected.	62S17
b	Orthorhombic: $a = 5.408 \text{ \AA}$, $b/a = 1.006$, $c = 41.05 \text{ \AA}$ at RT. $\rho = 7.3 \cdot 10^3 \text{ kg m}^{-3}$.	62S15
5a	Dielectric constant: $\kappa = 150$ at RT.	62S17

Nr. 7A-19 $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$

1a	Ferroelectric activity of $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ was observed by AURIVILLIUS in 1962.	62A5	
b	phase	II	I
	state	F	P
	crystal system	orthorhombic	tetragonal
	Θ	325 °C	
	$a = 5.527 \text{ \AA}$, $b = 5.514 \text{ \AA}$, $c = 50.37 \text{ \AA}$ at RT.		62A5 63I5
3	Crystal structure: Fig. 896; Tab. 106.		
4	Temperature dependence of lattice parameter: Fig. 897.		
5a	Dielectric constant: Fig. 898. $\kappa' = 360$, $\kappa'' = 22$ at RT.		62A5
c	Remanent polarization: $P_r = 2 \cdot 10^{-4} \text{ C m}^{-2}$ at RT. Coercive field: $E_c = 1.0 \cdot 10^6 \text{ V m}^{-1}$ at RT.		62A5
14b	Switching: see Fig. 892; Tab. 105.		

Tab. 106. $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$. Fractional coordinates of atoms [62A5]. Space group of $I4/mmm$ was assumed.

$I4/mmm$	$(0, 0, 0; 1/2, 1/2, 1/2) +$	
4 Bi in 4(e):	$\pm 0, 0, z$:	$z = 0.2255$
4 (Bi, Ba) in 4(e):		$z = 0.0420$
4 (Bi, Ba) in 4(e):		$z = 0.1300$
2 Ti in 2(b):	$\pm 0, 0, 1/2$	
4 Ti in 4(e):		$z = 0.3370$
4 Ti in 4(e):		$z = 0.4185$
4 O in 4(c):	$0, 1/2, 0; 1/2, 0, 0$	
4 O in 4(d):	$0, 1/2, 1/4; 1/2, 0, 1/4$	
4 O in 4(e):		$z = 0.2962$
4 O in 4(e):		$z = 0.3378$
4 O in 4(e):		$z = 0.4593$
8 O in 8(g):	$\pm (0, 1/2, z; 1/2, 0, z)$	$z = 0.0815$
8 O in 8(g):		$z = 0.1630$

Nr. 7A-20 $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$

1a	Ferroelectric activity in $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ was observed by SUBBARAO in 1962.	62S17	
b	phase	II	I
	state	F	P
	crystal system	orthorhombic (possibly)	tetragonal
	Θ	310 °C	
	$\rho = 6.6 \cdot 10^3 \text{ kg m}^{-3}$. $a = 5.461 \text{ \AA}$, $b/a = 1.000$, $c = 49.70 \text{ \AA}$ at RT.		62S17 62S15

5a	Dielectric constant: Fig. 899. $\kappa = 400$ at RT. $\kappa = C/(T - \Theta_p)$, $C = 4.1 \cdot 10^5$ °K, $\Theta_p = 280$ °C.			62S17
c	Spontaneous polarization: $P_s = 6 \cdot 10^{-2}$ C m ⁻² at 235 °C.			62S17
7a	Piezoelectric constant: $d_{33} = 2.5 \cdot 10^{-12}$ C N ⁻¹ .			62S17
Nr. 7A-21 Sr ₂ Bi ₄ Ti ₅ O ₁₈				
1a	Ferroelectric activity in Sr ₂ Bi ₄ Ti ₅ O ₁₈ was observed by SUBBARAO in 1962.			62S17
b	phase	II	I	
	state	F	P	
	crystal system	orthorhombic (possibly)	tetragonal	
	Θ	285 °C		
	$\rho = 5.3 \cdot 10^3$ kg m ⁻³ . $a = 5.461$ Å, $b/a = 1.000$, $c = 48.80$ Å at RT.			62S15
5a	Dielectric constant: Fig. 900. $\kappa = 280$ at RT. $\kappa = C/(T - \Theta_p)$, $C = 0.47 \cdot 10^5$ °K, $\Theta_p = 255$ °C.			62S17
c	Spontaneous polarization: $P_s = 3.5 \cdot 10^{-2}$ C m ⁻² at 255 °C.			62S17
7a	Piezoelectric constant: $d_{33} = 2.5 \cdot 10^{-12}$ C N ⁻¹ .			62S17
Nr. 7A-22 Bi ₂ Ti ₄ O ₁₁				
1a	Dielectric anomaly associated with a phase transition was observed in Bi ₂ Ti ₄ O ₁₁ by SUBBARAO in 1962.			62S16
b	phase	III	II	65J4
	crystal system	monoclinic	monoclinic	
	space group	C2/c-C _{2h} [*]	C2/m-C _{2h} ^{**}	
	Θ	250*	1200*	°C
	$\rho = (6.12 \pm 0.02) \cdot 10^3$ kg m ⁻³ . $a = (14.612 \pm 0.006)$ Å, $b = (3.799 \pm 0.004)$ Å, $c = (14.946 \pm 0.006)$ Å, $\beta = (93.13 \pm 0.01)^\circ$ at RT.			*62S16 65J4 65J4
3	Crystal structure: $Z = 2$ in phase II. $Z = 4$ in phase III. Fig. 901, 902; Tab. 107.			65J4
4	Thermal expansion: Fig. 903.			
5a	Dielectric constant: Fig. 904.			
c	No hysteresis loops could be obtained between 25 °C and 290 °C.			62S16
Tab. 107. Bi ₂ Ti ₄ O ₁₁ . Atomic parameters at RT [65J4]				
Atom		<i>x</i>	<i>y</i>	<i>z</i>
O(1)		0.0	0.262 ± 0.012	0.250
O(2)		0.1828 ± 0.0024	0.246 ± 0.007	0.2207 ± 0.0024
O(3)		0.1408 ± 0.0024	0.256 ± 0.007	0.0338 ± 0.0024
O(4)		0.0814 ± 0.0024	0.760 ± 0.007	0.1259 ± 0.0024
O(5)		0.2662 ± 0.0024	0.747 ± 0.007	0.0880 ± 0.0024
O(6)		0.0546 ± 0.0024	0.770 ± 0.007	0.9221 ± 0.0024
Ti(1)		0.0530 ± 0.0006	0.250 ± 0.002	0.1406 ± 0.0006
Ti(2)		0.1461 ± 0.0006	0.759 ± 0.002	0.0162 ± 0.0006
Bi		0.3211 ± 0.00015	0.1747 ± 0.0005	0.1798 ± 0.00015
Thermal parameter $B = 0.33$ Å ² for all atoms. Coordinates and standard deviations in cell fractions.				
7B Complex compounds and solid solutions				
Nr. 7B-1 Bi _{1-x} Me ₂ ²⁺ Ti _{1-x} Nb _{1+x} O ₉ (Me ²⁺ = Ba, Sr, Pb)		1b	Lattice parameter: Fig. 905. Transition temperature: Fig. 906.	
		5	Dielectric constant: Fig. 907.	
Nr. 7B-2 Bi _{1-x} Me ₂ ²⁺ Ti _{2-x} Nb _x O ₁₂ (Me ²⁺ = Ba, Sr, Pb)		1b	Lattice parameter: Fig. 908. Transition temperature: Fig. 909.	
		5	Dielectric constant: Fig. 910.	
* The unit cell of phase II has about half the volume of the unit cell of phase III.				

Nr. 7B-3 $\text{Na}_{0.5}\text{Bi}_{1.5}\text{Ti}_4\text{O}_{15}$		
1a	Dielectric anomaly associated with a phase transition was reported by SUBBARAO in 1962.	62S17
b	phase	II I
	state	P
	crystal system	orthorhombic tetragonal
	Θ	650 °C
	$q = 6.3 \cdot 10^3 \text{ kg m}^{-3}$.	62S17
	$a = 5.427 \text{ \AA}$, $b/a = 1.006$, $c = 40.65 \text{ \AA}$ at RT.	62S15
5a	Dielectric constant: Fig. 911. $\kappa = 200$ at RT. $\kappa = C/(T - \Theta_p)$, $C = 0.79 \cdot 10^5 \text{ °K}$, $\Theta_p = 610 \text{ °C}$.	62S17
7a	Piezoelectric constant: $d_{33} = 1.0 \cdot 10^{-11} \text{ C N}^{-1}$.	62S17
Nr. 7B-4 $\text{K}_{0.5}\text{Bi}_{1.5}\text{Ti}_4\text{O}_{15}$		
1a	Dielectric anomaly associated with a phase transition was reported by SUBBARAO in 1962.	62S17
b	phase	II I
	state	P
	crystal system	orthorhombic tetragonal
	Θ	550 °C
	$q = 6.7 \cdot 10^3 \text{ kg m}^{-3}$.	62S17
	$a = 5.440 \text{ \AA}$, $b/a = 1.004$, $c = 41.15 \text{ \AA}$ at RT.	62S15
5a	Dielectric constant: Fig. 912. $\kappa = 140$ at RT. $\kappa = C/(T - \Theta_p)$, $C = 0.74 \cdot 10^5 \text{ °K}$, $\Theta_p = 515 \text{ °C}$.	62S17
7a	Piezoelectric constant: $d_{33} = 1.0 \cdot 10^{-11} \text{ C N}^{-1}$.	62S17
Nr. 7B-5 $(\text{Pb}_{1-x}\text{Ba}_x)\text{Bi}_2\text{Nb}_2\text{O}_9$ and $(\text{Pb}_{1-x}\text{Sr}_x)\text{Bi}_2\text{Nb}_2\text{O}_9$		
1b	Transition temperature: Fig. 913.	
5	Dielectric constant: Fig. 914.	
Nr. 7B-6 $(1-x)\text{Bi}_4\text{Ti}_3\text{O}_{15} - x\text{BaTiO}_3$		
5	Transition temperature: Fig. 915.	
Nr. 7B-7 $\text{Bi}_{4+x}\text{Pb}_{1-x}\text{Ti}_4\text{Ga}_x\text{O}_{15}$		
1a	Another formula for this solid solution is $(1-x)\text{PbBi}_4\text{Ti}_4\text{O}_{15} \cdot x\text{Bi}_2\text{Ti}_2\text{GaO}_{15}$. Properties of this solid solution were studied by SUBBARAO in 1962.	62S17
b	$x = 0.25$:	
	phase	II I
	state	P
	crystal system	orthorhombic (pseudo-tetragonal) tetragonal
	Θ	600 °C
	Pseudo-tetragonal cell parameter: $a = 3.842 \text{ \AA}$, $c = 41.40 \text{ \AA}$ at RT.	
	Dielectric constant: $\kappa = 180$ at RT; $\kappa = 3035$ at Θ .	
	$x = 0.5$:	
	phase	II I
	state	P
	crystal system	orthorhombic (pseudo-tetragonal) tetragonal
	Θ	620 °C
	Pseudo-tetragonal cell parameter: $a = 3.842 \text{ \AA}$, $c = 41.40 \text{ \AA}$ at RT.	62S17
	Dielectric constant: $\kappa = 179$ at RT; $\kappa = 1930$ at Θ .	

BRIEF ATTACHMENT U

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Date: March 1, 2005

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

FIRST SUPPLEMENTAL AMENDMENT

Sir:

In response to the Office Action dated July 28, 2004, please consider the
following:

ATTACHMENT U

STRUCTURE, PROPERTIES AND PREPARATION OF PEROVSKITE-TYPE COMPOUNDS

BY
FRANCIS S. GALASSO
United Aircraft Research Laboratories

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BRIEF ATTACHMENT V

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

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TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Date: March 1, 2005

Docket: YO987-074BZ

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Examiner: M. Kopec

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

FIRST SUPPLEMENTAL AMENDMENT

Sir:

In response to the Office Action dated July 28, 2004, please consider the
following:

ATTACHMENT V

ARKIV FÖR KEMI Band 1 nr 54

Communicated 15 September 1949 by ARNE WESTGREN and ARNE TISBLIUS

Mixed bismuth oxides with layer lattices

I. The structure type of $\text{CaNb}_2\text{Bi}_2\text{O}_9$

By BENGT AURIVILLIUS

With 5 figures in the text

In the course of a comprehensive investigation of mixed bismuth oxides, the system $\text{Bi}_2\text{O}_3-\text{TiO}_2$ was studied. At about 40 atomic % of TiO_2 a phase with a body-centered pseudo-tetragonal unit cell with $a = 3.84$ and $c = 32.8 \text{ \AA}$ was found. X-ray analysis (to be published later) seemed to show that the structure was built up of $\text{Bi}_2\text{O}_2^{2+}$ layers parallel to the basal plane, and sheets of composition $\text{Bi}_2\text{Ti}_3\text{O}_{10}^{2-}$. The atomic arrangement within the $\text{Bi}_2\text{Ti}_3\text{O}_{10}^{2-}$ sheets seemed to be the same as in structures of the perovskite type and the structure could then be described as consisting of $\text{Bi}_2\text{O}_2^{2+}$ layers between which double perovskite layers are inserted.

An attempt was then made to synthesize compounds where the $\text{Bi}_2\text{O}_2^{2+}$ layers alternate with single perovskite layers. The general formula for such compounds could be expected to be: $(\text{MeBi})_6\text{R}_4\text{O}_{18}$. In actual fact compounds with this structure could be prepared with Me: Na K Ca Ba Sr Pb R: Ti Nb Ta.

Procedure: Weighed amounts of the appropriate oxides or carbonates were mixed and heated in platinum or gold crucibles to about 1000°C . A number of compounds with the general formula $(\text{Bi, Me})_6\text{R}_4\text{O}_{18}$ were prepared. Out of these the following were found to have a body-centered tetragonal or pseudo-tetragonal unit cell. The real unit cells, however, appeared to be face-centered-orthorhombic.

Composition	Orthorhombic description			Pseudo-tetragonal description	
	a	b	c	a	c
$\text{Bi}_3\text{NbTiO}_9$	5.405	5.442	25.11	3.836	25.11
$\text{Bi}_3\text{TaTiO}_9$	5.402	5.436	25.15	3.832	25.15
$\text{CaBi}_2\text{Nb}_2\text{O}_9$	5.435	5.485	24.87	3.860	24.87
$\text{SrBi}_2\text{Nb}_2\text{O}_9$	5.504	5.504	25.05	3.892	25.05
$\text{SrBi}_2\text{Ta}_2\text{O}_9$	5.509	5.509	25.06	3.895	25.06
$\text{BaBi}_2\text{Nb}_2\text{O}_9$	5.533	5.533	25.55	3.912	25.55
$\text{PbBi}_2\text{Nb}_2\text{O}_9$	5.492	5.503	25.53	3.887	25.53
$\text{KBi}_6\text{Nb}_4\text{O}_{18}$	5.506	5.506	25.26	3.893	25.26
$\text{NaBi}_6\text{Nb}_4\text{O}_{18}$	5.47	5.47	26.94	3.87	26.94

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Single crystals were prepared from the $\text{PbBi}_2\text{Nb}_2\text{O}_9$ and $\text{Bi}_2\text{NbTiO}_9$ phases. Weissenberg photographs of $0kl$ and $1kl$ (pseudo-tetragonal cell) were taken. In the powder photographs of $\text{Bi}_2\text{NbTiO}_9$ (Table 6a) the reflections 110 , 211 , 215 , 220 and 310 were clearly split up. No cleavage was found for the reflections $10l$, $20l$, and $30l$, (in all cases pseudo-tetragonal indices). From this it was concluded that the structure might be described by means of orthorhombic unit cells, having the same c axes as the pseudo-tetragonal cells, and a and b axes equal to the diagonals of the pseudo-tetragonal cells. Using orthorhombic units the Weissenberg photographs register hkl and $h, h+2, l$. In Table 6a the $\sin^2 \theta$ of $\text{Bi}_2\text{NbTiO}_9$ are calculated on the assumption of an orthorhombic unit cell.

A few discrepancies occur between the intensities of the spots as found in the Weissenberg photographs (first layer) and in the powder photographs. In the Weissenberg photographs ($h, h+2, l$), no difference was found between reflections hkl and hhl . From the powder photographs it is seen that 024 might be < 204 and that $311 < 131$ and $3111 < 1311$. The reason might be the orientation of the powder.

 $\text{PbBi}_2\text{Nb}_2\text{O}_9$ phase

The powder photographs of $\text{PbBi}_2\text{Nb}_2\text{O}_9$ (Table 6b) could be explained assuming a tetragonal cell with $a = 3.887 \text{ \AA}$ and $c = 25.53 \text{ \AA}$, but for two lines being split up, which indicated an orthorhombic unit cell with axes $a = 5.492$, $b = 5.503$ and $c = 25.53 \text{ \AA}$. As in $\text{Bi}_2\text{NbTiO}_9$, it was thus assumed that the real symmetry is $D_{2h} - mmm$, though nothing in the Weissenberg photographs indicated a lower Laue symmetry than $D_{2h} - 4/mmm$. The observed density was 7.91 , thus allowing 4 formula units/unit cell ($d_{\text{calc.}} = 8.22$).

With the exception of the criterion for face-centering that hkl occurring only with h, k, l all odd or all even, no systematic extinctions were found. This is characteristic of the space groups D_{2h}^{22} , D_2^7 and C_{2h}^{12} .

Positions of the metal atoms

As the scattering factors for the Pb and the Bi atoms are almost the same, it makes no difference in the intensity calculations whether the Pb and the Bi atoms occupy separate positions or are mixed at random. Therefore no difference will be made between Pb and Bi; they will both be denoted by Me.

The intensities of the reflections seemed to depend mainly on the value of l (see Table 1a). It therefore seemed probable that at least the Me and the Nb atoms are placed along the lines: $(000; \frac{1}{2}\frac{1}{2}0; \frac{1}{2}0\frac{1}{2}; 0\frac{1}{2}\frac{1}{2}) + 00z$. The sum of $\sum I_{00l} \cos 2\pi lz$ and $\sum I_{11l} \cos 2\pi lz$ will under such conditions represent the Patterson function along $00z$. In Fig. 1a these sums are plotted as functions of z . It is seen from the graph that high maxima occur for $z = 0.20$ and $z = 0.40$.

The unit cell of $\text{PbBi}_2\text{Nb}_2\text{O}_9$ contains 12 Me atoms and 8 Nb atoms.

If the space groups are assumed to be D_{2h}^{22} , D_2^7 or C_{2h}^{12} a or b , the only way of placing 12 Me atoms on the lines $00z$ is in one 4-fold and one 8-fold position. With these assumptions the only 4-fold positions possible are 000 or $00\frac{1}{2}$.

The crystals in the vicinity of maximum tetragonal indices $10l, 11l, 20l$ have been determined.

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Table 1a

Weissenberg Photographs of $\text{PbBi}_2\text{Nb}_2\text{O}_9$. Cu K_α radiation

The crystals form very thin plates, and therefore considerable absorption occurs. Spots in the vicinity of the lines described by WELLS (2) will therefore be weakened. The regions of maximum absorption are denoted by dotted lines. In the tables 1, 2 and 3 pseudotetragonal indices are used, and observed and calculated intensities for the reflections: 001, 101, 111, 201, and 211 are given. With orthorhombic description these reflections would have been denoted by: 001, 021 or 201, 221, 131 or 311.

l	I_1	I_2	I_{00l}	$I_{\text{obs.}} I_{111}$	I_{201}
2	18	1.2		vw	vw
4	9.0	34	m^-	m	w
6	0.1	8.4	vw	m	—
8	25	14	m^-	w	w
10	350	340	vst	m^+	m
12	19	0.2	w	—	—
14	36	100	m^+	vw	w
16	9.6	4.8	vw	—	—
18	45	31	m	w	w
20	280	230	st	m^+	m^+
22	22	0.04	—	—	—
24	71	200	m^+	m	m^+
26	27	14	w	vw	vw
28	85	26	m^-	w	w
30	190	130	m	m	
32	25	8.4	w		

l	I_1	I_2	I_{101}	$I_{\text{obs.}} I_{211}$	
1	1.7	17	m	—	
3	20	6.3	m^-	vw	
5	380	370	vst	st	
7	18	0.0	—	—	
9	12	63	m	w	
11	3.2	5.3	—	—	
13	32	23	w	vw	
15	320	280	st	w	
17	20	0.2	—	—	
19	55	160	m^+	w^+	
21	18	7.8	vw	—	
23	61	32	m	w^+	
25	230	170	m^+	m	
27	24	1.7	—	—	
29	85	250	m^+		
31	48	23	w		

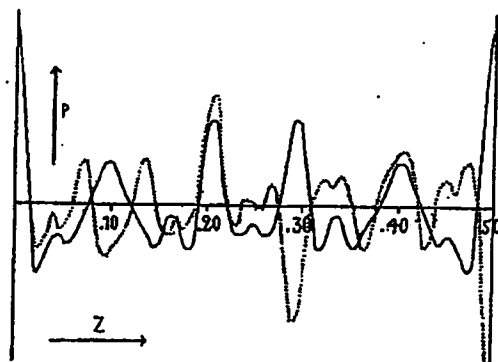
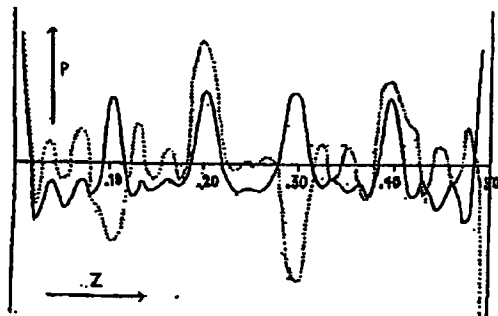
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Table 1b
Weissenberg Photographs of $\text{PbBi}_2\text{Nb}_2\text{O}_9$

Zero layer				First layer			
00l	I'_1	$I_{\text{obs.}}$	I'_2	21l	I'_1	$I_{\text{obs.}}$	I'_2
4	11	m ⁻	32	1	1.7	—	14
6	1.4	vw	1.4	3	18	vw	4.8
8	28	m ⁻	14	5	330	st	340
10	360	vst	360	7	18	—	0.4
12	45	w	11	9	23	w	67
14	50	m ⁺	88	11	4.8	—	3.6
16	6.3	vw	5.8	13	26	vw	23
18	70	m	38	15	300	w	280
20	280	st	230	17	13	—	0.3
22	25	—	0.4	19	42	w ⁺	150
24	58	m ⁺	250	21	14	—	7.8
26	21	w	10	23	66	w ⁺	36
28	85	m ⁻	21	25	210	m	170
30	240	m	120	27	23	—	2.9
32	17	w	6.8				
10l				11l			
10l	I'_1	$I_{\text{obs.}}$	I'_2	11l	I'_1	$I_{\text{obs.}}$	I'_2
1	1.0	m	8.4	2	18	vw	1.2
3	14	m ⁻	4.0	4	9.0	m	34
5	320	vst	340	6	0.1	m	8.4
7	16	—	0.5	8	25	w	14
9	24	m	67	10	350	m ⁺	340
11	6.3	—	2.0	12	19	—	0.2
13	24	w	24	14	36	vw	100
15	310	st	280	16	9.6	—	4.8
17	13	—	0.5	18	45	w	31
19	42	m ⁺	150	20	280	m ⁺	230
21	14	vw	7.8	22	22	—	0.0
23	64	m	38	24	71	m	200
25	210	m	170	26	27	vw	14
27	23	—	2.9	28	85	w	26
29	81	m ⁺	220	30	190	m	130
31	32	w	24				
20l							
20l	I'_1	$I_{\text{obs.}}$	I'_2				
2	12	vw	1.4				
4	10	w	36				
6	0.5	—	4.8				
8	31	w ⁻	14				
10	350	m	350				
12	41	—	7.8				
14	50	w ⁻	88				
16	6.3	—	6.3				
18	69	w	40				
20	280	m ⁺	230				
22	25	—	0.4				
24	59	m ⁺	240				
26	20	vw	11				
28	85	w	21				

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Figure 1a. Patterson function of $\text{PbV}_2\text{Bi}_2\text{Nb}_2\text{O}_{10}$ along $00z$ Full curve: $\sum I_{00l} \cos 2\pi lz$ Dotted curve: $\sum I_{11l} \cos 2\pi lz$ (orthorhombic indices).Figure 1b. Patterson function of $\text{Bi}_3\text{NbTiO}_{10}$ along $00z$

Of 8-fold positions only $\pm 00z$ is possible.

It was assumed arbitrarily that 4 Me occupy the position 000.

Using the distances found with the aid of the Patterson function, two possibilities for placing the Nb atoms arose:

- | | | |
|---------------------------|-------------|------------------------|
| 1. 8 Nb in $\pm 00\ 0.20$ | 4 Me in 000 | 8 Me in $\pm 00\ 0.40$ |
| 2. 8 Nb in $\pm 00\ 0.40$ | 4 Me in 000 | 8 Me in $\pm 00\ 0.20$ |

The two curves on the graph were added and the areas under the peaks at 0.20 and 0.40 calculated. The ratio 1.5:1 was found for 0.20/0.40.

In case 1, the ratio was calculated to be 0.91:1 and in case 2, 1.1:1 if the ratio $f_{\text{Nb}}/f_{\text{Bi}}$ was assumed to be 0.46. These figures cannot be compared directly with the observed ratio 1.5:1 since the zero level in figure 1 is of course uncertain. Case 2 agrees slightly better insofar as the peak at 0.20 is actually higher. It seemed, however, that the uncertainty in determining the areas was so large that case 1 could not be excluded by these measurements alone.

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Case 1

In calculating the structure amplitudes z_{Nb} was varied around 0.20 and z_{Me} around 0.40. The average ratio f_{Nb}/f_{Me} was assumed to be 0.46. The intensities were compared with calculated values of A^2 :

$A = 10 (\cos 2\pi lz_{Me} + 0.46 \cos 2\pi lz_{Nb} + 0.5) = 10 F/4 f_{Me}$. In this way the best values for the parameters were found to be:

$z_{Me} = 0.397 \pm 0.002$ and $z_{Nb} = 0.192 \pm 0.004$. In Table 1a I_{calc} is compared with the observed intensities.

Case 2

z_{Nb} was varied about 0.40 and z_{Me} around 0.20. The best values were found to be $z_{Nb} = 0.412 \pm 0.004$ and $z_{Me} = 0.202 \pm 0.002$.

The observed and calculated values are compared in Table 1a.

It was found that arrangement 2 accounted slightly better for the experimental data than 1. It must, however, be borne in mind that the intensity ratios of weak spots might be changed through the influence of the oxygen atoms and that this influence was neglected in the calculations. The differences did not seem to be as large as to allow a decision between 1 and 2. It was therefore tried to find possible oxygen positions both for 1 and 2. The results were then compared.

Case 1. Positions of the oxygen atoms

The positions of the metal atoms were assumed to be: $(000; 0\frac{1}{2}\frac{1}{2}; \frac{1}{2}0\frac{1}{2}; \frac{1}{2}\frac{1}{2}0) + 000 (4 Me_1) \pm 00 0.397 (8 Me_2) \pm 00 0.192 (8 Nb)$. Since all point positions of D_{2d}^{20} can be described by positions of D_2^7 or $C_{2v}^{18} a$, only D_2^7 and $C_{2v}^{18} a$ have been considered.

At first only D_2^7 will be discussed. If the interatomic distances O—O, Me—O and Nb—O should not be smaller than 2.5, 2.2 and 1.8 Å, oxygen atoms could only be situated in the following positions:

$$\begin{array}{llll} 4(b) 00\frac{1}{2} & 4(c) \frac{1}{2}\frac{1}{2}\frac{1}{2} & 4(d) \frac{1}{2}\frac{1}{2}\frac{1}{2} & 8(g) \pm 00z \\ 8(h) \frac{1}{2}\frac{1}{2}z; \frac{1}{2}\frac{1}{2}\frac{1}{2}-z & & & 0.086 \leq z \leq 0.122 \\ & 0.039 \leq |z| \leq 0.061 & & 0.262 \leq z \leq 0.311 \\ & 0.148 \leq |z| \leq 0.201 & & \\ 8(i) \frac{1}{2}y\frac{1}{2}; \frac{1}{2}\frac{1}{2}-y\frac{1}{2} & 8(j) x\frac{1}{2}\frac{1}{2}; \frac{1}{2}-x\frac{1}{2}\frac{1}{2} & & \\ y=0 & x=0 & & \end{array}$$

An attempt was made to find positions for the oxygen atoms giving approximately regular octahedra around Nb, since from known structures containing Nb^{5+} and O^{2-} this seemed to be the normal configuration $Nb^{5+} - O^{2-}$. The maximum distance of contact Nb—O was assumed to be 2.5 Å.

With these assumptions 8(g) and 8(h) are the only positions where oxygen atoms in contact with Nb can be situated.

With oxygen atoms in three 8-fold positions 8(h) the distances O—O would be too short. It then only remains to consider the case of oxygen atoms in two 8-fold positions 8(g) and two 8 fold positions 8(h). For the oxygen

atoms in contact with Nb, reasonable interatomic distances were obtained assuming: 8 O₂ in 8(g) $z_2 = 0.100$ 8 O₃ in 8(g) $z_3 = 0.264$ 8 O₄ in 8(h) $z_4 = 0.168$ 8 O₅ in 8(h) $z_5 = -0.168$. Even if small adjustments of these parameters are admitted for the remaining 4 O there is room only in the position $00\frac{1}{2}$ (O₁).

With these assumptions the distances would be:

Me ₁ -4 O ₁ = 2.75	Me ₂ -4 O ₂ = 2.75	Nb - O ₂ = 2.34
Me ₁ -2 O ₂ = 2.55	Me ₂ -2 O ₄ = 2.55	Nb - 2 O ₄ = 2.04
	Me ₂ -2 O ₅ = 2.55	Nb - O ₅ = 2.04
O ₄ -4 O ₅ = 2.74		Nb - O ₃ = 1.84
O ₃ -2 O ₄ = 2.60		
O ₃ -2 O ₅ = 2.60		
O ₁ -2 O ₂ = 2.55		

It is seen that the positions given might equally well be described by D_{2h}^{22} or if the pseudo-tetragonal unit cell ($a = 3.89$ $c = 25.53$ Å) is chosen by D_{4h}^{17} .

As $a \sim b$ and the positions of the oxygen atoms must be chosen from space considerations, the discussion will be the same for C_{2v}^{18} as for C_{2v}^{18} . For C_{2v}^{18} it is found that the oxygen atoms can be only in the planes $y = 0$ $y = 0.25 \pm 0.03$ $y = \frac{1}{2}$ and $y = 0.75 \pm 0.03$. For $y = 0$ or $\frac{1}{2}$, z must either be 0 or $\frac{1}{2}$ or lie between the limits $0.049 < |z| < 0.451$, otherwise the distance O-O will be < 2.5 Å. For $y = \frac{1}{4}$ or $\frac{3}{4}$, z must have the values 0, $\frac{1}{2}$, $\frac{1}{4}$ or $\frac{3}{4}$ or lie between the limits $0.049 < |z| < 0.201$ $0.299 < |z| < 0.451$.

In figure 2a sections of the unit cell are made for $y = 0$ and $y = \frac{1}{2}$. Possible regions with space group C_{2v}^{18} are denoted in the figure by shaded areas. For these areas the distances O-O ≥ 2.5 Me-O ≥ 2.2 and Nb-O ≥ 1.8 Å.

With space group C_{2v}^{18} it thus seems that no basically new atomic positions are obtained, although this symmetry allows the atoms to be slightly shifted from the positions of D_2^7 .

In Table 1 the intensities have been calculated from the parameters found and compared with the observed ones. (The calc. intensities are denoted by I_1). The mode of calculation is shown by the calculation of I_{001} . $I = A^2$.

$A = 10 (0.5 + \cos 2\pi lz_{Me} + (f_{Nb}/f_{Me}) \cos 2\pi lz_{Nb} + (f_O/f_{Me}) (0.5 + \cos 2\pi lz_2 + \cos 2\pi lz_3 + 2 \cos 2\pi lz_4))$. Since the ratios f_{Nb}/f_{Me} and f_O/f_{Me} vary with $\sin \theta/\lambda$ they were interpolated from values given in the *International Tables* (1).

Case 2. Positions of the oxygen atoms

The positions of the metal atoms were assumed to be: $(000; \frac{1}{2} \frac{1}{2} 0; 0 \frac{1}{2} \frac{1}{2}; \frac{1}{2} 0 \frac{1}{2}) + 000$ (4 Me₁) ± 00 0.202 (8 Me₂) ± 00 0.412 (8 Nb).

With D_2^7 the following positions are available for the oxygen atoms 4(b) $00\frac{1}{2}$

8(g) $\pm 00z$	8(h) $\frac{1}{4} \frac{1}{4} z, \frac{1}{4} \frac{1}{4} -z$
$0.086 \leq z \leq 0.116$	$0.039 \leq z \leq 0.161$
$0.288 \leq z \leq 0.342$	
4(c) $\frac{1}{4} \frac{1}{4} \frac{1}{4}$	4(d) $\frac{1}{4} \frac{1}{4} \frac{1}{4}$
	16(k) $xyz, \bar{x}\bar{y}z, x\bar{y}\bar{z}, \bar{x}y\bar{z}$
	$x = 0$ $x = 0.25 \pm 0.03$
	$y = 0.25 \pm 0.03$ or $y = 0$
	$z \sim 0.135$.

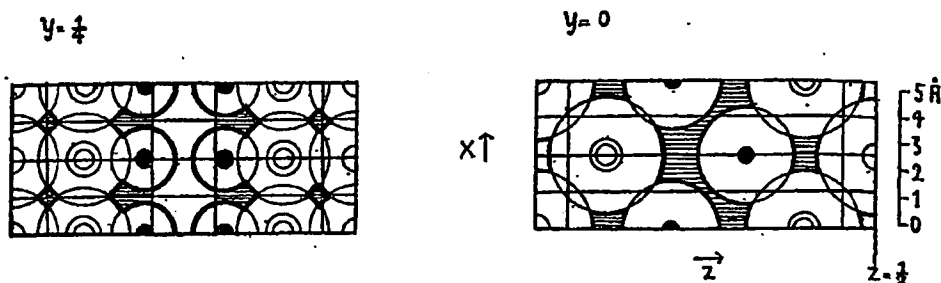
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Figure 2 a (see Case 1 in the text.)

The projection of the positions of the Nb, Me₁ and Me₂ atoms on the planes $y=0$ and $y=\frac{1}{4}$ are denoted by: black circles, white circles and double circles respectively.

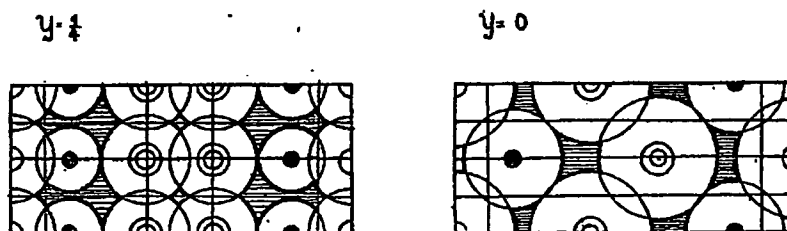


Figure 2 b (see Case 2 in the text.)

It was found that oxygen atoms in the positions 4(c), 4(d) or 16(k) could not be part of an octahedron around Nb. With O in the remaining positions 4(b), 8(g) and 8(h), octahedra around Nb might be achieved in the following ways: ($1.8 \leq \text{Nb}-\text{O} \leq 2.5$).

With oxygen atoms in three 8-fold positions 8(h), it seemed impossible to find positions for the remaining 12 oxygen atoms giving O-O distances ≤ 2.5 Å.

With two 8-fold positions 8(h) + 4(b) + one 8-fold position 8(g) the following positions were assumed for oxygen atoms in contact with Nb:

$$\begin{array}{lll} 4 \text{ O}_1 \text{ in } 4(b) & 8 \text{ O}_2 \text{ in } 8(g) & z = 0.324 \\ 8 \text{ O}_3 \text{ in } 8(h) & z = 0.088 & 8 \text{ O}_4 \text{ in } 8(h) \quad z = -0.088. \end{array}$$

For the remaining 8 oxygen atoms there was only room in the positions 4(c) and 4(d). (O₅, O₆).

With the above assumptions the distances would be:

$$\begin{array}{lll} \text{Me}_1 - 4 \text{ O}_1 = 2.75 & \text{Me}_2 - 2 \text{ O}_5 = 2.29 & \text{Nb} - \text{O}_1 = 2.24 \\ \text{Me}_1 - 4 \text{ O}_3 = 2.96 & \text{Me}_2 - 2 \text{ O}_6 = 2.29 & \text{Nb} - 2 \text{ O}_3 = 1.94 \\ \text{Me}_1 - 4 \text{ O}_4 = 2.96 & \text{Me}_2 - 4 \text{ O}_2 = 2.82 & \text{Nb} - 2 \text{ O}_4 = 1.94 \\ & & \text{Nb} - \text{O}_2 = 2.24 \\ \\ \text{O}_5 - 4 \text{ O}_6 = 2.75 & \text{O}_2 - 2 \text{ O}_5 = 2.70 & \text{O}_2 - 2 \text{ O}_3 = 2.96 \\ \text{O}_3 - 4 \text{ O}_4 = 2.75 & \text{O}_2 - 2 \text{ O}_6 = 2.70 & \text{O}_2 - 2 \text{ O}_4 = 2.96 \\ & \text{O}_1 - 4 \text{ O}_3 = 2.96 & \\ & \text{O}_1 - 4 \text{ O}_4 = 2.96 & \end{array}$$

The above positions might be equally well described by D_{2h}²³ or if a pseudotetragonal unit cell is assumed ($a = 3.89$ c = 25.53) by D_{4h}¹⁷.

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In Figure 2b sections are made of the unit cell for $y = 0$ and $y = \frac{1}{2}$ showing the positions possible for the oxygen atoms if the space group C_{2v}^{18} is assumed. Possible regions are denoted by shaded areas. It was found that only with oxygen atoms situated near the positions given above, could octahedra of O around all Nb atoms and reasonable distances Nb-O be attained.

Thus no new arrangements were found when space group C_{2v}^{18} was assumed. In Table 1 the intensities are calculated from the parameters given above. The calculated intensities are denoted by I_2 . The mode of calculation is the same as was used in case 1. It is seen from the Table that both 1 and 2, in which cases the influence of the oxygen atoms was neglected, account fairly well for the experimental data. From this follows that the calculated intensities I_1 and I_2 , where regard was taken to the O atoms, do not differ much either. Although the ratio 211:213 (see Table 1 (pseudo-tetragonal indices)) is best described by 1', 2' on the whole seemed to satisfy the observed intensities best (see for instance the intensity ratios 112:114 116:118 202:204 101:103 and 107:109). No definite conclusions could however be drawn from the study of $PbBi_2Nb_2O_9$ alone.

 Bi_3NbTiO_9

Just as for $PbBi_2Nb_2O_9$, there was nothing in the Weissenberg photographs to indicate a lower Laue symmetry than $D_{4h}-4/mmm$. From the powder photographs (Table 6a) it is however seen that the actual unit cell is orthorhombic with axes $a = 5.405$ $b = 5.442$ $c = 25.11$ Å.

The intensities of the spots in the Weissenberg photographs indicate that the metal atoms are probably placed on the lines $00z$. The Patterson function (Fig. 1b) showed high maxima at 0.20 and 0.40. If the same assumptions are made as for $PbBi_2Nb_2O_9$, the following arrangements seemed to be possible:

A. 4 Nb in 000	B. 4 Ti in 000	C_1 4 Bi in 000
8 BiTi in $\pm 00z_1$	8 BiNb in $\pm 00z_1$	8 NbTi in $\pm 00z_1$
8 BiTi in $\pm 00z_2$	8 BiNb in $\pm 00z_2$	8 Bi in $\pm 00z_2$
C_2 4 Bi in 000		
8 NbTi in $\pm 00z_2$	$z_1 \sim 0.20$	$z_2 \sim 0.40$
8 Bi in $\pm 00z_1$		

The areas under the peaks at 0.20 and 0.40 were calculated as for $PbBi_2Nb_2O_9$, and the ratio 0.20/0.40 was found to be 1.4. The calculated ratios for A, B, C_1 and C_2 were 1.0, 1.0, 0.84 and 1.2. The area ratio for C_2 agreed best with the observed one. The differences are however small, so that all alternatives were considered. The intensities were calculated as for $PbBi_2Nb_2O_9$. The ratios f_{Ti}/f_{BiNb} , f_{Nb}/f_{BiTi} and f_{NbTi}/f_{Bi} were assumed to be 0.26, 0.57 and 0.34. The calculated and observed intensities for A and B are compared in Table 2. In these calculations the influence of the oxygen atoms was neglected. The best agreement was found for

	z_1	z_2
A	0.198	0.400
B	0.196	0.400

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Table 2
Weissenberg photographs of $\text{Bi}_3\text{NbTiO}_9$.

h	I_A	I_B	I_{00l}	$I_{\text{obs.}} I_{11l}$	I_{20l}
2	4.0	12	—	vw	vw
4	7.3	22	m	st	m ⁺
6	2.3	5.3	w	st	m
8	7.3	22	m	w	m
10	510	440	st	st	st
12	1.4	2.6	w	—	vw
14	15	52	m ⁺	vw	w
16	0.2	0.0	w	vw	—
18	11	30	m ⁺	w	vw
20	500	400	st	st	m ⁺
22	0.1	0.4	—	—	—
24	27	94	m	m	m
26	0.5	2.0	w	m	m
28	14	31	m	m ⁺	m ⁺
30	490	350	m	m ⁺	—
h	I_A	I_B	I_{10l}	I_{21l}	
1	4.4	12	st	m ⁺	
3	5.8	17	m	vw	
5	520	450	vst	vst	
7	2.6	6.3	—	—	
9	11	35	m	m	
11	0.8	1.4	w	w	
13	9.0	27	vw	w	
15	510	420	st	w	
17	0.6	0.3	—	—	
19	20	70	w	w	
21	0.0	0.5	w	w	
23	12	31	m	m	
25	500	380	m ⁺	m ⁺	
27	0.0	3.2	—	—	
29	34	120	m	—	
31	1.4	4.4	m	—	

From Table 2 it is seen that A and B account quite well for the observed intensities.

With A and B, Bi and Ti or Bi and Nb would occupy the same point position. This seemed *a priori* unlikely and if it was assumed that $\text{Bi}_3\text{NbTiO}_9$ and $\text{PbBi}_2\text{Nb}_2\text{O}_9$ were built up in the same way, arrangements A and B would imply that Pb, Bi and Nb were distributed over one point position, in $\text{PbBi}_2\text{Nb}_2\text{O}_9$. Therefore, although arrangements A and B cannot be excluded from intensity discussions alone, they seem very improbable and will not be dealt with in the following.

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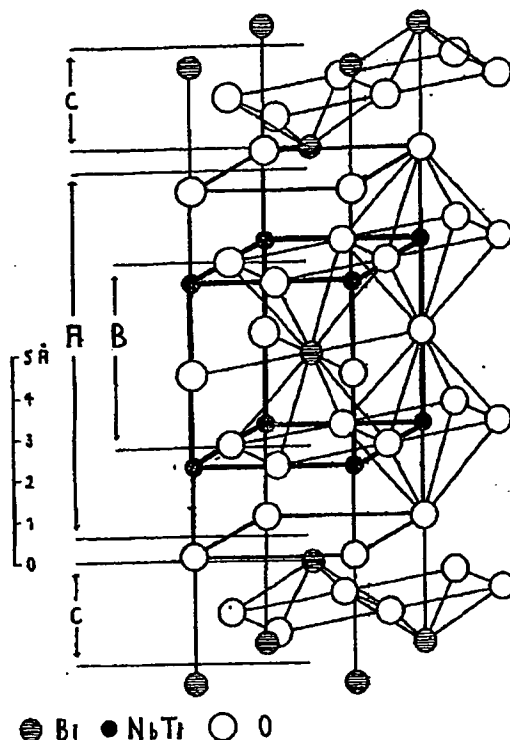


Figure 3.

One half of the pseudo-tetragonal unit cell of $\text{Bi}_2\text{NbTiO}_9$ (from $z \approx 0.25$ to $z \approx 0.75$). A denotes the perovskitic layer BiNbTiO_7 , C Bi_2O_3 layers and B the unit cell of a hypothetical perovskite structure $\text{BiNb}_{0.5}\text{Ti}_{0.5}\text{O}_3$.

Case C_1

The following positions were assumed: 4 Bi in 000, 8 Bi in $\pm 00\ 0.396$, 8 NbTi in $\pm 00\ 0.192$. By the same arguments as used for $\text{PbBi}_2\text{Nb}_2\text{O}_9$ the following positions were arrived at:

$$\begin{array}{lll} 4\ \text{O}_1\ \text{in}\ 00\frac{1}{2} & 8\ \text{O}_2\ \text{in}\ \pm 00\ 0.092 & 8\ \text{O}_3\ \text{in}\ \pm 00\ 0.268 \\ 8\ \text{O}_4\ \text{in}\ \frac{1}{4}\frac{1}{4}z; \frac{1}{4}\frac{1}{4}\frac{1}{2}-z & z = 0.164 & \\ 8\ \text{O}_5\ \text{in}\ \frac{1}{4}\frac{1}{4}z; \frac{1}{4}\frac{1}{4}\frac{1}{2}-z & z = -0.164. & \end{array}$$

In Table 3 the intensities are calculated from these parameters.

Case C_2

4 Bi in 000, 8 Bi in $\pm 00\ 0.200$ and 8 NbTi in $\pm 00\ 0.412$ were assumed. In case 2' (see $\text{PbBi}_2\text{Nb}_2\text{O}_9$) the parameters for the oxygen atoms would be 4 O_1 in $00\frac{1}{2}$, 8 O_2 in $\pm 00\ 0.324$, 4 O_3 in $\frac{1}{4}\frac{1}{4}\frac{1}{2}$,

$$\begin{array}{lll} 4\ \text{O}_6\ \text{in}\ \frac{1}{4}\frac{1}{4}\frac{1}{2} & 8\ \text{O}_4\ \text{in}\ \frac{1}{4}\frac{1}{4}z; \frac{1}{4}\frac{1}{4}\frac{1}{2}-z & z = 0.088 \\ & 8\ \text{O}_5\ \text{in}\ \frac{1}{4}\frac{1}{4}z; \frac{1}{4}\frac{1}{4}\frac{1}{2}-z & z = -0.088 \end{array}$$

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Table 3
Weissenberg photographs of $\text{Bi}_2\text{NbTiO}_9$

Zero layer				First layer			
00l	$I_{C'_1}$	$I_{\text{obs.}}$	$I_{O'_1}$	21l	$I_{C'_1}$	$I_{\text{obs.}}$	$I_{C'_1}$
4	13	m	36	1			
6	0.5	w	10	3	2.6	m ⁺	22
8	48	m	16	5	35	vw	6.3
10	310	st	330	7	290	vst	300
12	46	w	12	9	19	—	1.0
14	38	m ⁺	59	11	27	m	55
16	2.6	w	29	13	3.6	w	18
18	100	m ⁺	48	15	52	w	26
20	240	st	240	17	270	w	270
22	12	—	0.5	19	6.8	—	0.8
24	42	m	140	21	45	w	90
26	29	w	42	23	14	w	40
28	100	m	35	25	110	m	46
30	190	m	150		200	m ⁺	200
10l	$I_{C'_1}$	$I_{\text{obs.}}$	$I_{O'_1}$	11l	$I_{C'_1}$	$I_{\text{obs.}}$	$I_{C'_1}$
1	2.0	st	17	2	34	vw	2.6
3	29	m	5.3	4	2.9	st	41
5	270	vst	300	6	6.8	st	69
7	17	—	1.2	8	62	w	22
9	29	m	56	10	360	st	310
11	5.8	w	15	12	14	—	1.0
13	49	vw	28	14	29	vw	76
15	270	st	270	16	10	vw	40
17	5.3	—	0.6	18	64	w	16
19	44	w	92	20	250	st	210
21	16	w	38	22	21	—	0.0
23	110	m	46	24	66	m	92
25	200	m ⁺	200	26	32	m	61
27	4.4	—	1.2	28	130	m ⁺	27
29	65	m	110	30	150	m ⁺	200
31	41	m	76				
20l	$I_{C'_1}$	$I_{\text{obs.}}$	$I_{O'_1}$				
2	18	vw	2.9				
4	12	m ⁺	37				
6	0.1	m	16				
8	48	m	17				
10	300	st	320				
12	33	vw	5.8				
14	37	w	58				
16	2.6	—	31				
18	100	vw	45				
20	240	m ⁺	240				
22	12	—	0.5				
24	42	m	140				
26	29	m	45				
28	100	m ⁺	35				

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In Table 3 the intensities are calculated with these assumptions.. It is seen from the Table that with C_1 the order of the reflections 101:103, 211:213, 202:204 and 107:109 are reversed. The same result was obtained if the influence of the oxygen atoms was neglected. If z_{Bi} and z_{NbTi} were varied around 0.396 and 0.192 so as to give correct ratios for some of these reflections, large discrepancies occurred for other reflections. With C_2 the intensities turned out to be of the right order. There are however a few discrepancies. 00 20 is certainly stronger than 0018 and $00\ 30 > 0028$, but the calculated ratios seem to be too large. On the whole the agreement is however good.

Thus if the X ray data for only one of $PbBi_2Nb_2O_9$ or Bi_3NbTiO_9 were considered, different atomic arrangements appeared to be possible, whereas only one seems to explain the observed data both for $PbBi_2Nb_2O_9$ and Bi_3NbTiO_9 .

With orthorhombic description the positions will be:

$D_{2h}^{22} - mmm$

$(000; 0\frac{1}{2}\frac{1}{2}; \frac{1}{2}0\frac{1}{2}; \frac{1}{2}\frac{1}{2}0) +$

4 Bi_1 (Me_1) in 4 (a) 000

8 Bi_2 (Me_2) in 8 (i) $\pm 00\ 0.200$ (0.202)

8 NbTi (Nb) in 8 (i) $\pm 00\ 0.412$ (0.412)

4 O_1 in 4 (b) $00\frac{1}{2}$

8 O_2 in 8 (i) $00\ 0.324$ (0.324)

8 O_3 in 8 (f) $\frac{1}{2}\frac{1}{2}\frac{1}{2}; \frac{1}{2}\frac{1}{2}\frac{1}{2}$

16 O_4 in 16 (g) $\frac{1}{2}\frac{1}{2}z; \frac{1}{2}\frac{1}{2}\bar{z}; \frac{1}{2}\frac{1}{2}z; \frac{1}{2}\frac{1}{2}\bar{z}$
 $z = 0.088.$

With pseudo-tetragonal description the positions will be:

$D_{4h}^{17} - I\ 4/mmm$

$(000; \frac{1}{2}\frac{1}{2}\frac{1}{2}) +$

2 Bi_1 (Me_1) in 2 (a) 000

4 Bi_2 (Me_2) in 4 (e) $\pm 00\ 0.200$ (0.202)

4 NbTi (Nb) in 4 (e) $\pm 00\ 0.412$ (0.412)

2 O_1 in 2 (b) $00\frac{1}{2}$

4 O_2 in 4 (e) $\pm 00\ 0.324$ (0.324)

4 O_3 in 4 (d) $0\frac{1}{2}\frac{1}{2}; \frac{1}{2}0\frac{1}{2}$

8 O_4 in 8 (g) $\pm (0\frac{1}{2}z; \frac{1}{2}0z) z = 0.088.$

Table 4

Values of the tolerance factor, t , for different compounds having the $CaBi_2Nb_2O_9$ structure.

Compound	$t \cdot 100$
Bi_3NbTiO_9	91
Bi_3TaTiO_9	91
$CaBi_2Nb_2O_9$	91
$SrBi_2Nb_2O_9$	99
$SrBi_2Ta_2O_9$	99
$BaBi_2Nb_2O_9$	106
$PbBi_2Nb_2O_9$	101
$NaBi_2Nb_4O_{18}$	91
$KBi_2Nb_4O_{18}$	97

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Table 5

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Powder photographs of $\text{CaBi}_2\text{Nb}_2\text{O}_9$ and $\text{SrBi}_2\text{Nb}_2\text{O}_9$. Cr K radiation. Pseudo-tetragonal indices.

$\text{CaBi}_2\text{Nb}_2\text{O}_9$				
hkl	$I_{\text{obs.}}$	I_{α}	I_{β}	I_{γ}
006	—	8.4	0.8	0.01
008	m	61	9.6	0.6
114+00 10	(m)	230	230	230
00 12	—	0.5	19	47
00 14	vw	29	46	56
00 16	vw	2.6	0.6	4.0
00 18	w	100	34	13
101	—	1.2	0.5	2.9
103	st	36	1.4	1.4
105	vst	200	200	200
107	w	21	0.3	7.8
109	vvw	18	32	43
10 11	—	7.0	0.2	0.5
10 13	m ⁺	79	19	4.4
20 10+10 15	(st)	160	160	160
21 11+10 17	(w)	22	0.2	9.0
112	—	26	0.04	4.8
00 10+114	(m)	4.4	14	22
116	w	4.4	17	26
118	m	69	13	1.7
204+11 10	(st)	200	200	200
11 12	—	22	0.1	8.4
11 14	w	41	61	72
202	w	27	0.1	4.4
11 10+204	(st)	3.6	13	20
206	w	3.2	0.04	1.4
215+208	(st)	59	9.0	0.5
10 15+20 10	(st)	220	220	220
20 12	vw	1.4	15	41
211	w	0.1	2.3	6.3
213	w	38	2.0	1.0
208+216	(st)	210	210	210
217	—	21	0.3	7.8
219	vvw	18	33	43
10 17+21 11	(w)	4.4	0.01	1.4

$\text{SrBi}_2\text{Nb}_2\text{O}_9$				
hkl	$I_{\text{obs.}}$	I_{α}	I_{β}	I_{γ}
006	—	3.2	0.1	0.2
008	vw	45	11	2.6
114+00 10	(m)	260	260	260
00 12	vw	0.2	16	35
00 14	m	42	68	64
00 16	—	0.3	1.4	4.4
00 18	w	83	36	18
00 20	st	160	160	160

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ARKIV FÖR KEMI. Bd 1 nr 54

Table 5 (cont.)

i. Pseudo

<i>hkl</i>	<i>I</i> _{obs.}	<i>I</i> _α	<i>I</i> _β	<i>I</i> _γ
101	—	0.0	2.0	4.0
103	vw	24	2.0	0.1
105	st	230	240	230
107	—	12	0.01	3.6
109	w	28	42	49
10 11	—	2.3	0.01	0.8
10 13	m	61	20	8.4
20 10+10 15	(st)	190	200	200
β 00 20+220+10 17	(m)	13	0.01	4.0
10 19	m	88	110	120
112	—	16	0.3	1.7
00 10+114	(m)	10	20	26
116	vw	10	22	29
118	w	52	14	4.4
11 10	st	230	240	230
11 12	—	13	0.0	3.6
11 14	w	56	74	81
11 16	—	0.1	4.0	8.4
11 18	m	40	10	2.3
202	—	17	0.4	1.4
204	—	9.0	19	24
206	—	0.5	0.6	2.3
β 11 14+208	(w)	43	10	2.3
10 15+20 10	(st)	250	260	250
β 21 13+20 12	(vw)	0.01	12	29
20 14	w	42	58	64
20 16	—	0.2	1.7	4.8
211	w	0.6	4.8	7.8
213	w	26	2.6	0.01
215	st	240	240	240
217	—	12	0.01	3.6
219	vw	27	42	49
21 11	—	1.2	0.4	2.0
21 13	m	59	19	7.8
20 10+21 15	(st)	190	180	190

One half of the pseudo-tetragonal unit cell is pictured in figure 3. As mentioned in the discussion on $\text{PbBi}_2\text{Nb}_2\text{O}_9$, it was impossible in this phase to determine how Pb and Bi are distributed over the point positions 000 and 00 0.202. It therefore seemed of interest to try to determine the positions of Ca, Sr, Ba and K in the compounds $\text{CaBi}_2\text{Nb}_2\text{O}_9$, $\text{SrBi}_2\text{Nb}_2\text{O}_9$, $\text{BaBi}_2\text{Nb}_2\text{O}_9$ and $\text{KBi}_2\text{Nb}_2\text{O}_9$. As the cell dimensions of the Pb, Ca, Sr, Ba and K compounds do not differ much it was assumed that the parameters of $\text{PbBi}_2\text{Nb}_2\text{O}_9$ are also valid for the other compounds. There were three extreme ways of distributing Ca, Sr, Ba and K over the positions 000 and 00 0.202:

- α Only Bi in 00 202
- β Random distribution
- γ Only Bi in 000.

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Table 6a

Powder photographs of $\text{Bi}_3\text{NbTiO}_9$. Cr K radiation.

Orthorhombic indices.

hkl	$10^4 \sin^2 \theta_{\text{calc.}}$	$10^4 \sin^2 \theta_{\text{obs.}}$	$I_{\text{obs.}}$	hkl	$10^4 \sin^2 \theta_{\text{calc.}}$	$10^4 \sin^2 \theta_{\text{obs.}}$	$I_{\text{obs.}}$	hkl	$I_{\text{obs.}}$
111	0914	0909	m	02 14	5858	5874	m	101	
113	1080	1072	w+	20 14	5878	5990	vw	103	
008	1333	1319	w+	—	—	6129	w+	008	
115	1414	1413	vst	13 9	6128	6175	w+	105	
020	1774	1767	m+	31 9	6172	6250	vw	110	
200	1796	1790	m	—	—	6573	vw	00 10	
00 10	2083	2078	m	22 12	6569	6747	vw	114	
204	2129	2131	w	00 18	6747	6961	w	β 109	
β 119	2136	2324	vw	13 11	6961	7097	m	116	
—	—	—	—	040	7097	7182	m	109	
026	2524	2530	m	02 16	7105	7388	w	β 200	
206	2546	2546	m	20 16	7127	7648	w	00 12	
119	2580	2586	m	042	7180	7836	vw	118	
—	—	2739	vw	400	7186	8005	w	10 11	
028	3107	3129	w	β 240	7357	8330	m	200	
208	3129	3415	w	β 420	7420	8411	m	11 10	
11 11	3413	3523	w	044	7430	8430	st	00 14	
—	—	3576	st	22 14	7652	8558	st	10 13	
220	3570	3648	vw	046	7847	8888	m	211	
222	3653	3860	st	406	7935	8963	m	208	
β 11 13	3654	4089	w	13 13	7960	9105	st	215	
02 10	3857	4236	vw	31 13	8004	9156	vst	10 15	
20 10	3879	4320	w	331	8054	9189	m	20 10	
00 14	4082	4414	w	00 20	8330	9264	m		
β 135	4103	4454	vw	11 19	8411	9709	w		
—	—	4504	vw	048	8430	9712	w		
226	4320	4623	w	20 18	8543				
11 13	4412	4676	w	335	8554				
131	4462	4896	w	240	8887				
311	4506	4956	st	22 16	8901				
β 11 15	4521	5006	st	420	8959				
133	4628	5579	st	242	8970				
313	4672	5581	st	13 15	9127				
β 22 10	4679	5652	st	31 15	9171				
228	4903			04 10	9180				
135	4962			40 10	9288				
315	5006			424	9292				
—	—			426	9709				
11 15	5579			339	9720				
22 10	5653								

The intensities were calculated for these possibilities by calculations similar to those for $\text{PbBi}_2\text{Nb}_2\text{O}_9$, and compared with the observed ones. See Table 5. It was found that in no case did γ explain the observed intensities. For the Sr, Ba and K compounds the observed intensities did not permit any decision between α and β . For $\text{CaBi}_2\text{Nb}_2\text{O}_9$, however, only α seemed to give correct intensities. It was therefore concluded that the compounds discussed have the α arrangement.

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Table 6b

Powder photographs of $\text{PbBi}_2\text{Nb}_2\text{O}_9$. Cr K radiation.

Pseudo-tetragonal indices.

$I_{\text{obs.}}$	hkl	$10^4 \sin^2 \theta_{\text{calc.}}$	$10^4 \sin^2 \theta_{\text{obs.}}$	$I_{\text{obs.}}$	hkl	$10^4 \sin^2 \theta_{\text{calc.}}$	$10^4 \sin^2 \theta_{\text{obs.}}$	$I_{\text{obs.}}$
m	101	0889	0892	vw	1114	5682	5699	m
vw	103	1050	1052	vww	219	5974	5990	m
w+	008	1288	1285	vww	0018	6520	6529	w
w+	105	1372	1371	vst	0020	6663	6664	vww
vww	110	1738	1763	m	1017	6685		
vww	0010	2012	2019	m	1116	6889	6924	m
vw	114	2060	2068	vww	β 305	6903		
w	β 109	2069			220	6950	6934	m
	116	2462	2469	m			6976	m
m	109	2499	2499	m	2014	7419	7435	m
	β 200	2877	2881	m	2113	7744	7749	m
m	0012	2898			301	7839	7846	vw
	118	3026	3028	w	0020	8049	8052	m
w	1011	3304	3300	vww	1019	8133	8131	m+
	200	3475	3475	st	228	8238	8268	vw
w	1110	3750	3755	st	1118	8258		
	0014	3944	3946	w+	305	8332	8339	m+
w	1013	4269	4270	w+	310	8688	8673	m+
vww	211	4364	4365	vww			8690	m+
	208	4763	4770	vww	2115	8872	8874	st
w	215	4847	4850	st	2210	8962	8980	m
	1015	5397	5416	st	314	9010		
m	2010	5487	5493	st	309	9449	9450	vww

The structure of $\text{Bi}_2\text{NbTiO}_9$ is thus built up of $\text{Bi}_2\text{O}_3^{2+}$ layers between which BiNbTiO_7^{2-} layers are inserted. The structure may be looked upon as a perovskite structure where perovskite layers are separated by $\text{Bi}_2\text{O}_3^{2+}$ layers. This view was supported by the fact that in all cases where the above structure was observed the radii of the ions in the layers lying between the $\text{Bi}_2\text{O}_3^{2+}$ layers would allow for the formation of a perovskite structure. If the tolerance factor t is calculated from the ionic radii of the elements constituting the layers between the $\text{Bi}_2\text{O}_3^{2+}$ layers, it is found to lie between the limits 0.9 and 1.1 (see Table 4), the same limits within which perovskite structures are found to be stable.

t was calculated from the formula: $1.06 (R_A + R_O) = 0.95 t \sqrt{2} (R_B + R_O)$. (See (3).)

$$A = (K + \text{Bi})/2 \text{ Ca, Sr, Ba etc.}$$

$$B = (\text{Nb} + \text{Ti})/2 (\text{Ta} + \text{Ti})/2 \text{ Nb, Ta.}$$

In the calculations case a was assumed. For calculating t the following values for the ionic radii were used: Bi^{3+} 1.00, Ba^{2+} 1.39, Sr^{2+} 1.20, Ca^{2+} 1.02, Pb^{2+} 1.26, Na^{+} 0.97, K^{+} 1.33, Nb^{5+} 0.69, Ta^{5+} 0.69, Ti^{4+} 0.66 and O^{2-} 1.36. If, for instance, 1 K + 1 Bi are distributed over one 2-fold position the radius of (K, Bi) was taken as $(r_K + r_{\text{Bi}})/2$.

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The structure proposed for $\text{CaBi}_2\text{Nb}_2\text{O}_9$ reminds one of the structure of beyerite $\text{CaBi}_2\text{O}_3(\text{CO}_3)_2$ described by LAGERCRANTZ and SILLÉN (4). The unit cell of beyerite is body-centered tetragonal with $a = 3.767$ and $c = 21.690$ Å. The positions of the Ca and the Bi atoms in beyerite are Ca 000 and Bi ± 00 0.19 (space group D_{2h}^{17}), as compared with $a = 3.860$ $c = 24.87$, Ca in 000 and Bi in ± 00 0.20 for $\text{CaBi}_2\text{Nb}_2\text{O}_9$.

The "rotating" CO_3^{2-} groups in beyerite correspond to octahedral sheets $\text{Nb}_4\text{O}_{12}^{4-}$ in $\text{CaBi}_2\text{Nb}_2\text{O}_9$. Following the notations given by LAGERCRANTZ and SILLÉN (4) the structure described above might also be denoted by X_{11} .

SUMMARY

A series of tetragonal or pseudo-tetragonal phases of general composition $(\text{Bi}, \text{Me})_6\text{R}_4\text{O}_{18}$ have been investigated.

Me: Na, K, Ca, Sr, Ba, Pb.

R: Nb, Ta, Ti.

The positions of the Me and R atoms were determined from the observed intensities and the positions of the O atoms were deduced from space considerations.

The following structure is proposed:

D_{2h}^{23} - F *mmm*

$(000; 0\frac{1}{2}\frac{1}{2}; \frac{1}{2}0\frac{1}{2}; \frac{1}{2}\frac{1}{2}0) +$
 4 Bi in 4 (a) 000
 8 Bi in 8 (c) ± 00 0.200
 8 NbTi in 8 (c) ± 00 0.412
 4 O in 4 (b) $00\frac{1}{2}$
 8 O in 8 (c) ± 00 0.324
 8 O in 8 (f) $\frac{1}{4}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{1}{4}\frac{3}{4}$
 16 O in 16 (j) $\frac{1}{4}\frac{1}{4}z; \frac{1}{4}\frac{1}{4}\bar{z}; \frac{1}{4}\frac{3}{4}z; \frac{1}{4}\frac{3}{4}\bar{z}$ $z = 0.088$.

From intensity calculations it was found that Ca in $\text{CaBi}_2\text{Nb}_2\text{O}_9$ and Sr, Ba and K in the corresponding compounds are probably situated in the position 000. The proposed structure is built up of $\text{Bi}_2\text{O}_7^{2-}$ layers alternating with single perovskite layers. The resemblance to the structure of beyerite is pointed out.

I wish to thank Professor L. G. SILLÉN for valuable discussions concerning this work.

Stockholms Högskola, Institute of Inorganic and Physical Chemistry, June 1949.

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Tryckt den 31 december 1949

Uppsala 1949. Almqvist & Wiksells Boktryckeri AB

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BRIEF ATTACHMENT W

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Date: March 1, 2005

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

FIRST SUPPLEMENTAL AMENDMENT

Sir:

In response to the Office Action dated July 28, 2004, please consider the
following:

ATTACHMENT W

ARKIV FÖR KEMI Band 1 nr 58

Communicated 15 September 1949 by ARNE WESTGREN and ARNE TISELIUS

Mixed bismuth oxides with layer lattices

II. Structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$

By BENGT AURIVILLIUS

With 5 figures in the text

By means of X ray analysis it has been found that the crystal structures of a number of bismuth oxyhalides consist of $\text{Bi}_2\text{O}_3^{2+}$ layers alternating with layers of halogen ions (1, 2). In all these cases the symmetry was found to be tetragonal and the lengths of the a axes almost constant ≈ 3.8 Å.

On making an X ray study of the system Bi_2O_3 — TiO_2 a phase (of composition about 40 atomic % TiO_2) was found, the powder photographs of which could be explained by assuming a pseudo-tetragonal cell with $a = 3.84$ and $c = 32.8$ Å. It seemed of interest to make a closer study of this phase since the cell dimensions and composition seemed to indicate a layer lattice with $\text{Bi}_2\text{O}_3^{2+}$ layers, but of a type hitherto uninvestigated.

Procedure: Weighed amounts of Bi_2O_3 (puriss) and TiO_2 (puriss) were mixed and heated to about 1100°C for some hours in a weighed platinum crucible. After cooling the crucible was weighed again and the composition calculated by assuming that the loss of weight could be ascribed to the volatility of Bi_2O_3 . Powder photographs of various preparations in the system Bi_2O_3 — TiO_2 indicated that there is a phase with a body-centered pseudo-tetragonal unit cell with $a = 3.841$ and $c = 32.83$ Å at compositions about 40 mole % TiO_2 . It was, however, impossible to get samples which were quite free from impurities so the powder photographs always contained a few extra lines.

The lines 21 $\bar{1}$, 22 $\bar{1}$ and 31 $\bar{1}$ were found to be split up. No cleavage was, however, found for the lines 10 $\bar{1}$, 20 $\bar{1}$ and 30 $\bar{1}$. This could be explained by assuming a face-centered orthorhombic unit cell with the same c axis as the pseudo-tetragonal cell and with its a and b axes equal to the diagonals ($a\sqrt{2}$) of the pseudo cell.

The orthorhombic axes will be: $a = 5.410$ $b = 5.448$ $c = 32.84$ Å. The observed density (40 mole % TiO_2) is 7.85. If the composition is assumed to be $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (43 mole % TiO_2) and 4 formula units are assumed per unit cell the calculated density will be 8.04 which agrees fairly well with the observed value.

Single crystals, thin plates, were picked out and Weissenberg photographs (zero layer and first layer) were taken around the 3.84 axes, thus registering $h0l$ and $h1\bar{l}$ (pseudo cell) or hhl and $h, h+2, l$ (orthorhombic cell).

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Though there was nothing in the Weissenberg photographs to indicate lower Laue symmetry than $D_{4h} - 4/mmm$, it was — as has already been mentioned — found from the powder photographs that the real symmetry was not higher than orthorhombic (Laue symmetry $D_{2h} - mmm$).

Except for the extinctions following from the face-centering (hkl occurring only for h, k, l all odd or even) no systematic extinctions were found, which is characteristic of the space groups C_{2v}^{18} , D_2^7 and D_{2h}^{28} .

Positions of the bismuth atoms

Since the intensities of hkl with h, k, l all odd on one side and the intensities of hkl with h, k, l all even on the other side appeared to vary in the same way with l (see Table 1), it seemed probable that at least the bismuth atoms are situated on the lines: $(000; \frac{1}{2}\frac{1}{2}0; 0\frac{1}{2}\frac{1}{2}; \frac{1}{2}0\frac{1}{2}) + 00z$. The sum of $\sum I_{00l} \cos 2\pi lz$ and $\sum I_{11l} \cos 2\pi lz$ will under such conditions represent the Patterson function along $00z$. These two sums are pictured in figure 1. It is seen from the graph that high maxima occur at $z = 0.144, 0.280$ and 0.428 . If C_{2v}^{18} is not considered, only the following positions on the lines $00z$

Table 1

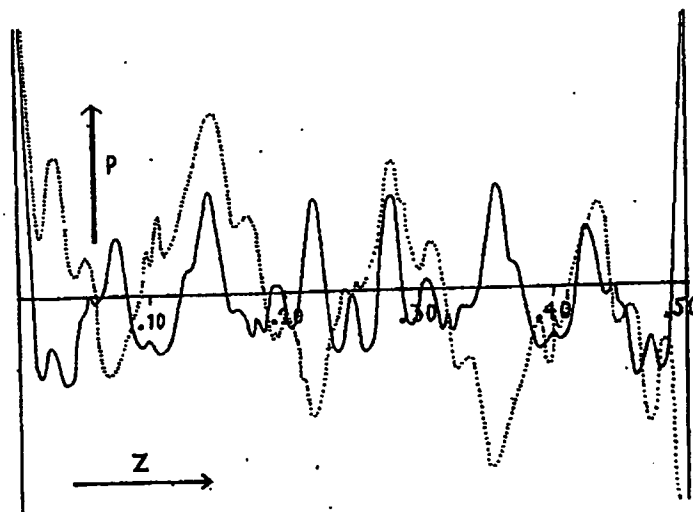
Weissenberg Photographs of $Bi_4Ti_3O_{12}$. Cu K_α radiation

l	I _{calc.}	I _{obs.}				l	I _{calc.}	I _{obs.}		
		00	20 or 02	22	42 or 24			11	31 or 13	33
2	4.4		—	vw	—	1	130	vst	m	m
4	20		w	w	—	3	14	w	—	—
6	85	m	m	m	w	5	18	m	vw	—
8	180	m	m	m	w ⁺	7	390	vst	m ⁺	m ⁺
10	8.4	w	m	vw	—	9	0.01	—	—	—
12	42	m	m	w	—	11	26	w	vw	vw
14	360	vst	m	m	m	13	42	w	vw	vw
16	3.6	m ⁺	—	vw	—	15	230	w	vw	—
18	32	m	w	vw	—	17	4.4	—	—	—
20	12	m	w	—	—	19	74	m	vw	vw
22	260	st	st	m	m	21	300	st	m	w
24	2.0	w	w	vw	—	23	14	m	w	vw
26	110	m	st	st	m ⁺	25	37	m	m	w
28	240	m	st	st	st	27	0.09	—	—	—
30	27	w	m	m	m	29	280	st	st	st
32	40	m	st	m	st	31	0.6	w	w	—
34	7.8	vw	w	vw	—	33	150	st	st	st
36	280	m	vst	vst	—	35	170	st	st	—
38	0.1	vw	w	vw	—	37	41	m	m	—
40	190	m	vst	—	—	39	40	st	—	—
42	110	m	—	—	—	41	36	m	—	—

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Figure 1. Patterson function of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ along $00z$

$$\text{Full curve: } \sum I_{00l} \cos 2\pi lz$$

$$\text{Dotted curve: } \sum I_{11l} \cos 2\pi lz \quad (\text{orthorhombic indices})$$

are possible for the Bi atoms: The two 4-fold positions 000 and $00\frac{1}{2}$ and the 8-fold positions $\pm 00z$. Assuming that the unit cell contains 16 Bi it was found that the observed maxima in the graph could be explained by assuming that the 16 Bi atoms are situated in two 8-fold positions $\pm 00z$. In this way three possibilities arose:

- a. $z_1 = 0.215$ $z_2 = 0.356$
- b. $z_1 = 0.072$ $z_2 = 0.356$
- c. $z_1 = 0.072$ $z_2 = 0.215$.

If the influence of the Ti and the O atoms is neglected the Patterson maxima will have the following relative weights:

	a	b	c
0.144	2	1	3
0.280	1	3	2
0.428	3	2	1

If the two curves in figure 1 are added and the areas under the peaks calculated, the ratio of $(0.144):(0.280):(0.428)$ is found to be: $4.4:2.6:1.0$. Now, these figures cannot be directly compared with the figures given above, since the zero level in the graph is unknown. It is, however, seen that the observed order of magnitude of the peaks (0.144) (0.280) and (0.428) is the same as

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that calculated for c. Case c was therefore assumed, and z_1 and z_2 were varied around 0.072 and 0.215. The observed intensities were found to agree quite well with those calculated for $z_1 = 0.067 \pm 0.004$ and $z_2 = 0.211 \pm 0.004$. In Table 1 the observed intensities are compared with intensities calculated as follows: $I = A^2$ $A = 10 (\cos 2\pi l z_1 + \cos 2\pi l z_2) = 10 F/4 f_{Bi}$. In Table 1 the lines of maximum absorption (see (4)) are indicated by dotted lines. If allowance is made for the polarisation factors and the absorption effect (4), it is seen that for h, k, l all odd the observed and calculated intensities agree quite well. For h, k, l all even the calculated ratios of 0016:0018 and 2216:2218 are inversed in comparison with the observed ratios. This might be due to the influence of the Ti and the O atoms.

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Positions of the Ti atoms

With the formula assumed the unit cell contains 12 Ti atoms. If the space group $C_{2v}^{18}c$ is not considered, the only 4-fold positions possible are:

- 4 (a) $x00$ or $0y0$ ($C_{2v}^{18} a$ or b), 4 (a) 000 4 (b) $00\frac{1}{2}$ (D_2^7, D_{2h}^{23}),
4 (c) $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ 4 (d) $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ (D_2^7)

The positions 000 , $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ seemed very improbable since the distance Bi—Ti would then be only 2.2–2.4 Å. For the remaining positions $00\frac{1}{2}$, $x00$ (or $0y0$) x (or y) must lie within the limits 0.38–0.62, if the minimum distance Bi—Ti is assumed to be 3.0 Å. If the distance Ti—Ti is assumed to be ≥ 3.0 Å, only 4 Ti can be situated in 4-fold positions and the remaining 8 Ti must occupy one 8-fold position. Of 8-fold positions the following seemed to be possible:

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the follow

- 8 (d) $x0z$, $x0\bar{z}$ (or $0yz$, $0y\bar{z}$) $C_{2v}^{18} a$ or b , 8 (g) $\pm 00z$ (D_2^7, D_{2h}^{23}),
8 (h) $\frac{1}{2}\frac{1}{2}z$, $\frac{1}{2}\frac{1}{2}\bar{z}$ (D_2^7)

Thus there seemed to be two ways of arranging the Ti atoms:

1. 4 Ti_1 in $00\frac{1}{2}$, 8 Ti_2 in $\frac{1}{2}\frac{1}{2}z$, $\frac{1}{2}\frac{1}{2}\bar{z}$ $0.133 \leq z \leq 0.147$
2. 4 Ti_1 in $00\frac{1}{2}$, $x00$ (or $0y0$) $0.38 \leq x \leq 0.62$ (or $0.32 \leq y \leq 0.68$)
8 Ti_2 in $\pm 00z$ $0.324 \leq z \leq 0.398$, $x0z$, $x0\bar{z}$ (or $0yz$, $0y\bar{z}$)
 $0.38 \leq x \leq 0.62$ (or $0.38 < y < 0.62$) $0.102 \leq z \leq 0.176$

Two regio

Both for 1 and 2 the parameters are chosen as to make the distances Bi—Ti ≥ 3.0 Å. The region possible for the Ti_2 atoms — assuming arrangement 2 — is shown by the shaded area in figure 2.

By calculating the intensities of 001 for various z_{Ti} values, it was found that the calculated ratio 0016:0018 (see the discussion on the Bi positions) was best for $z \sim 0.13_0$ or 0.37_0 .

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The intensities of the spots in the Weissenberg photographs were then calculated for the arrangements 1 and 2 but no decision between 1 and 2 could be made by comparison with the observed intensities. It was therefore tried to find possible arrangements for the O atoms with both 1 and 2.

Case 1

Space group D_2^7 and the following positions for the metal atoms were assumed:

8 Bi₁ in 8 (g) $z_1 = 0.067 \pm 0.004$ 8 Bi₂ in 8 (g) $z_2 = 0.211 \pm 0.004$
 4 Ti₁ in 4 (b) $00\frac{1}{2}$ 8 Ti₂ in 8 (h) $0.133 \leq z \leq 0.147$

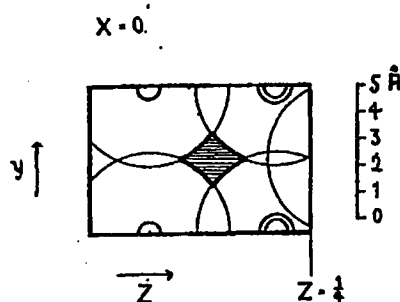


Figure 2.

By assuming that the distances $\text{Bi}-\text{O} \geq 2.2$, $\text{Ti}-\text{O} \geq 1.8$ and $\text{O}-\text{O} \geq 2.5$ Å, the following positions were found possible for the O atoms:

4 (a) 000 4 (c) $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ 4 (d) $\frac{1}{4}\frac{1}{4}\frac{3}{4}$
 8 (g) $\pm 00z$ 8 (h) $\frac{1}{4}\frac{1}{4}z; \frac{1}{4}\frac{1}{4}\frac{1}{2}-z$
 $0.130 \leq z \leq 0.148$ $0 \leq |z| \leq 0.040$
 $0.274 \leq z \leq 0.445$ $-0.183 \leq z \leq -0.095$

16 (k) $xyz; \bar{x}\bar{y}z; x\bar{y}\bar{z}; \bar{x}y\bar{z}$

$x \approx 0$ $y \approx 0$
 $y = 0.27$ or $x = 0.27$

Two regions are possible:

$z = 0.113$ (for $z_{\text{Ti}} = 0.147$) and $z = 0.165$ (for $z_{\text{Ti}} = 0.132$)

No combinations of these positions could be found giving reasonable distances and octahedra around the Ti atoms, as is the case in previously investigated structures containing Ti^{4+} and O^{2-} . Arrangement 1 seemed therefore improbable.

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Case 2

The positions of the metal atoms are assumed to be:

$$8 \text{ Bi}_1 \text{ in } \pm 00z_1 \quad z_1 = 0.067 \pm 0.004 \quad 8 \text{ Bi}_2 \text{ in } \pm 00z_2 \quad z_2 = 0.211 \pm 0.004$$

$$4 \text{ Ti}_1 \text{ in } 00\frac{1}{2}, x00 \text{ (or } 0y0) \quad 0.38 \leq x, y \leq 0.62 \quad 8 \text{ Ti}_2 \text{ in } \pm 00z, \\ 0.324 \leq z \leq 0.398$$

$$x0z; x0\bar{z} \text{ (or } 0yz; 0y\bar{z}) \quad 0.38 \leq x, y \leq 0.62 \\ 0.102 \leq z \leq 0.176$$

At first only space group D_2^7 was considered (Ti_1 in $00\frac{1}{2}$ and Ti_2 in $\pm 00z$). The following positions were found possible for the O atoms making the same assumptions as in case 1:

$$\begin{array}{lll} 4 \text{ (a) } 000 & 4 \text{ (c) } \frac{1}{4}\frac{1}{4}\frac{1}{4} & \\ 4 \text{ (d) } \frac{1}{4}\frac{1}{4}\frac{1}{4} & 8 \text{ (g) } \pm 00z & 8 \text{ (h) } \frac{1}{4}\frac{1}{4}z; \frac{1}{4}\frac{1}{4}\bar{z} - z \\ & 0.130 \leq z \leq 0.148 & 0 < |z| < 0.040 \\ & 0.379 \leq z \leq 0.445 & 0.095 < |z| < 0.183 \\ & 0.274 \leq z \leq 0.343 & \\ 16 \text{ (k) } xyz; x\bar{y}z; x\bar{y}\bar{z}; x\bar{y}\bar{z} & & \\ x = 0.25 \pm 0.02 & \text{or} & y = 0.25 \pm 0.02 \\ y \sim 0 & & x \sim 0 \\ & & 0.114 < z < 0.163 \end{array}$$

It was tried to find positions for the O atoms so that Ti_1 and Ti_2 would be surrounded by regular or almost regular octahedra of O atoms with distances $1.8 \leq \text{Ti}-\text{O} \leq 2.5$ Å. For O atoms in contact with Ti_1 , the following point positions are possible: 8 (h) $0 < |z| < 0.040$, 8 (g) $0.424 \leq z \leq 0.445$. With 8 O situated at $\frac{1}{4}\frac{1}{4}0$; $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ and 8 O at ± 00 0.442 regular octahedra of O would surround Ti_1 . It, therefore, seemed probable that oxygen atoms are situated near these positions.

For oxygen atoms in contact with Ti_2 , the following positions are possible:

$$\begin{array}{ll} 8 \text{ (g}_1\text{)} \quad 0.379 \leq z_1 \leq 0.445 & 8 \text{ (h)} \quad 0.095 \leq |z| \leq 0.183 \\ 8 \text{ (g}_2\text{)} \quad 0.274 \leq z_2 \leq 0.343 & 16 \text{ (k)} \quad 0.114 \leq z \leq 0.163 \end{array}$$

With one set of oxygen atoms situated at 8 (h) or 16 (k), every Ti_2 atom will be in contact with two oxygen atoms, while if oxygen atoms are situated at 8 (g_1) or 8 (g_2), Ti_2 will be in contact with only one oxygen atom. It was

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found that only one set of oxygen atoms could occupy the positions 16 (k), 8 (g_1) and 8 (g_2), while at most 32 oxygen atoms could be situated in positions 8 (h). The following arrangements allowing Ti_2 to be in contact with 6 O are possible:

- a. 16 O (k) + 8 O (h) + 8 O (h)
- b. 16 O (k) + 8 O (g_1) + 8 O (g_2) + 8 (h)
- c. 8 O (h) + 8 O (h) + 8 O (h)
- d. 8 O (h) + 8 O (h) + 8 O (g_1) + 8 O (g_2)

With a and b no combination of positions could be found, giving octahedra of oxygen atoms around Ti_2 .

c. With 8 O in $\frac{1}{2}\frac{1}{2}0$; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, 8 O in 00 0.442 and 24 O in positions 8 (h) ($z_1 \approx 0.102$ $z_2 \approx -0.139$ $z_3 \approx 0.177$) so as to form octahedra of oxygen atoms around Ti_1 and Ti_2 , there was room for the remaining 8 O atoms only in the position $\pm 00z$ $z = 0.274$ or in the positions 4 (c) + 4 (d). With these arrangements, however, the distances O—O would be short (≈ 2.4 Å).

With d, positions for the oxygen atoms could be chosen, allowing reasonable distances and giving octahedra of oxygen atoms around Ti_2 . Arrangement d was, therefore, preferred to the arrangements a, b and c.

The following parameters were assumed for oxygen atoms in contact with Ti_1 or Ti_2 :

- $8 O_1$ in 8 (h) $z = 0$
 $8 O_2$ in 8 (g) $z = 0.436$
 $(z_{Ti_1} = 0.372)$ $8 O_3$ in 8 (g) $z = 0.308$
 $8 O_4$ in 8 (h) $z = 0.128$
 $8 O_7$ in 8 (h) $z = -0.128$

Even if these parameters are varied considerably around the values given, room for the remaining 8 O is left only in the positions 4 (c) and 4 (d) (O_5, O_6).

The positions arrived at might also be described with space group $D_{2h}^{23} - F m m m$ as follows:

- $8 O_1$ in 8 (e) $\frac{1}{2}\frac{1}{2}0$; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$
 $8 O_2$ in 8 (f) $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$
 $8 O_3$ in 8 (i) $\pm 00z$ $z = 0.436$
 $8 O_4$ in 8 (i) $\pm 00z$ $z = 0.308$
 $16 O_5$ in 16 (j) $\frac{1}{2}\frac{1}{2}z$; $\frac{1}{2}\frac{1}{2}\bar{z}$;
 $\frac{1}{2}\frac{1}{2}z$; $\frac{1}{2}\frac{1}{2}\bar{z}$
 $z = 0.128$

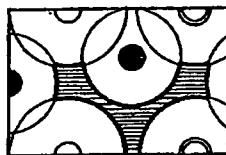
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The distances and coordination will be:

$\text{Bi}_1 - 4 \text{O}_1 = 2.92$	$\text{Ti}_2 - \text{O}_3 = 2.10$	$\text{Ti}_1 - 4 \text{O}_1 = 1.92$
$\text{Bi}_1 - 4 \text{O}_3 = 2.72$	$\text{Ti}_2 - \text{O}_4 = 2.10$	$\text{Ti}_1 - 2 \text{O}_3 = 2.10$
$\text{Bi}_1 - 4 \text{O}_5 = 2.76$	$\text{Ti}_2 - 4 \text{O}_5 = 1.92$	
$\text{Bi}_2 - 4 \text{O}_2 = 2.79$	$\text{O}_1 - 4 \text{O}_1 = 2.71$	
$\text{Bi}_2 - 4 \text{O}_4 = 2.79$	$\text{O}_3 - 4 \text{O}_1 = 2.83$	
$\text{Bi}_2 - 4 \text{O}_5 = 2.29$	$\text{O}_4 - 4 \text{O}_2 = 2.70$	
	$\text{O}_4 - 4 \text{O}_5 = 2.83$	
	$\text{O}_5 - 4 \text{O}_5 = 2.71$	

No new combinations were found if the space group D_{2h}^{23} was assumed instead of D_2^I .

$x=0$



$x=\frac{1}{4}$

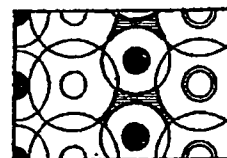
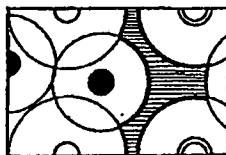


Figure 3 a.

$x=0$



$x=\frac{1}{4}$



Figure 3 b.

Since $a \approx b$ and the positions of the O atoms must be chosen from space considerations, it does not matter whether space group $C_{2v}^{18} a$ or b is assumed. $C_{2v}^{18} b$ was assumed arbitrarily. It was found that oxygen atoms could only be situated in the planes $x=0$, $x=0.25 \pm 0.02$, $x=\frac{1}{2}$ and $x=0.75 \pm 0.02$. Thus the following positions are possible:

$$\begin{array}{lll}
 4 \text{ (a) } 0y0 & 8 \text{ (b) } \frac{1}{4}y\frac{1}{4}; \frac{1}{4}y\frac{3}{4} & 8 \text{ (c) } 0yz; 0y\bar{z} \\
 8 \text{ (d) } xyz; \bar{x}y0 & 16 \text{ (e) } xyz; \bar{x}y\bar{z}; \bar{x}yz; x\bar{y}\bar{z} & \\
 x=0.25 \pm 0.02 & x=0.25 \pm 0.02 &
 \end{array}$$

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Table 2

Weissenberg Photographs of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. Cu K_α radiation

Zero Layer

0 0 l	I _{calc.}	I _{obs.}	2 0 l	I _{calc.}	I _{obs.}
6	56	m	2	1.0	vvw
8	61	m	4	12	w
10	12	w	6	59	m
12	58	m	8	81	m
14	450	vst	10	12	vvw
16	88	m ⁺	12	55	w
18	30	m	14	440	m
20	19	m ₋	16	64	vvw
22	200	st	18	31	vvw
24	27	w	20	19	—
26	120	m	22	200	m
28	230	m	24	26	vw
30	62	w	26	120	st
32	140	m ₋	28	230	st
34	4.0	vvw	30	62	m ₋
36	300	m	32	120	m
38	9.0	vw	34	4.0	vvw
40	110	m	36	290	vst
42	93	m	38	8.0	vw
1 0 l	I _{calc.}	I _{obs.}	3 0 l	I _{calc.}	I _{obs.}
1	52	vst	1	69	m
3	7.0	w	3	8.0	—
5	17	m ₋	5	18	—
7	470	vst	7	470	m ⁺
9	2.0	—	9	3.0	—
11	23	w	11	22	vw
13	46	w	13	45	vw
15	120	w	15	130	—
17	23	—	17	21	—
19	98	m	19	93	vw
21	320	st	21	320	w
23	36	m	23	36	vw
25	52	m	25	53	w
27	0.6	—	27	0.8	—
29	270	st	29	270	st
31	19	w	31	19	—
33	110	st			
35	140	st			
37	53	m			
39	75	st			
41	44	m			

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Table 2 (cont.)

First Layer

111	I _{calc.}	I _{obs.}	311	I _{calc.}	I _{obs.}
2	1.0	—	2	1.0	—
4	12	w	4	12	—
6	64	m	6	66	w
8	220	m	8	180	w ⁺
10	15	m ⁻	10	14	—
12	57	m ⁻	12	58	—
14	410	m	14	410	m
16	15	—	16	16	—
18	41	w	18	40	—
20	20	w	20	19	—
22	220	st	22	220	m
24	2.0	w	24	3.0	—
26	98	st	26	98	m ⁺
28	210	st	28	220	st
30	47	m	30	47	m
32	74	st	32	67	st
34	9.0	w			
36	310	vst			
38	4.0	w			
40	180	vst			
101	I _{calc.}	I _{obs.}	211	I _{calc.}	I _{obs.}
5	17	w	1	67	m
7	470	vst	3	8.0	—
9	2.0	vw	5	18	vw
11	23	m	7	470	m ⁺
13	46	m	9	2.0	—
15	120	m ⁺	11	23	vw
17	23	w	13	46	vw
19	98	m ⁺	15	130	vw
21	320	st	17	22	—
23	36	m	19	96	vw
25	52	m	21	320	m
27	0.6	—	23	36	w
29	270	st	25	50	m
31	19	w	27	0.8	—
33	110	st	29	270	st
35	140	st	31	19	w
37	53	m	33	110	st
39	75	st	35	140	st
41	44	st	37	53	m

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Table 3

Powder Photographs of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. Cr K radiation, orthorhombic description

hkl	$10^4 \sin^2 \theta_{\text{calc.}}$	$10^4 \sin^2 \theta_{\text{obs.}}$	$I_{\text{obs.}}$	hkl	$10^4 \sin^2 \theta_{\text{calc.}}$	$10^4 \sin^2 \theta_{\text{obs.}}$	$I_{\text{obs.}}$
008	0779	0771	st	11 19	5282	5292	m
111	0903	0895	m	22 12	5314		
115	1195	1188	vw	02 18	5710	5734	vw
—	—	1288	m	20 18	5735		
—	—	1336	w	00 22	5887	5892	m
117	1487	1480	vst	13 11	5900		
—	—	1614	vw	22 14	5946	5949	m
00 12	1752	1752	m	31 11	5950		
020	1769			11 21	6255	6267	st
200	1794	1790	w	02 20	6635		
024	1964	1952	vw	20 20	6660	6664	vw
β 00 14	1974	1974	m	22 18	6676		
204	1989			040	7074	7070	vw
00 14	2384	2384	vst	13 15	7165	7172	m
028	2548			400	7174		
208	2573	2565	st	31 15	7215	7221	m
11 13	2947	2947	m	402	7223		
β 220	2953			11 23	7326	7335	w
02 10	2985			22 18	7503	7511	w
β 11 15	3003	3005	w	046	7512		
20 10	3010			02 22	7656	7674	m
00 16	3114	3115	m	20 22	7681		
02 12	3521	3538	vw	00 26	8223	8223	w
20 12	3546			11 25	8494	8495	w
220	3562	3567	m	337	8611	8611	m
11 15	3628	3638	m	20 24	8801		
00 18	3941	3942	w	13 19	8819	8806	vw
226	4000	4006	w	04 12	8826		
02 14	4153			240	8868	8859	w
β 137	4159	4171	st	31 19	8869		
20 14	4178			242	8917		
β 317	4200			40 12	8926	8934	vw
228	4341	4333	w	420	8943		
11 17	4406	4418	vw	22 22	9449	9458	st
131	4440	4428	vw	04 14	9458		
311	4482	4490	vw	00 28	9537	9551	m
00 20	4866	4880	w	40 14	9558		
02 16	4883			248	9647	9652	vw
20 16	4908	4923	w	428	9722	9714	vw
β 22 14	4922			13 21	9792	9785	w
137	5024	5029	m				
317	5074	5078	m				

The positions of the Ti atoms are assumed to be:

$$4 \text{ Ti}_1 \text{ in } 4 \text{ (a)} \quad 0.38 \leq y_1 \leq 0.62$$

$$8 \text{ Ti}_2 \text{ in } 8 \text{ (c)} \quad 0.38 \leq y_2 \leq 0.62 \quad 0.102 \leq z_2 \leq 0.176$$

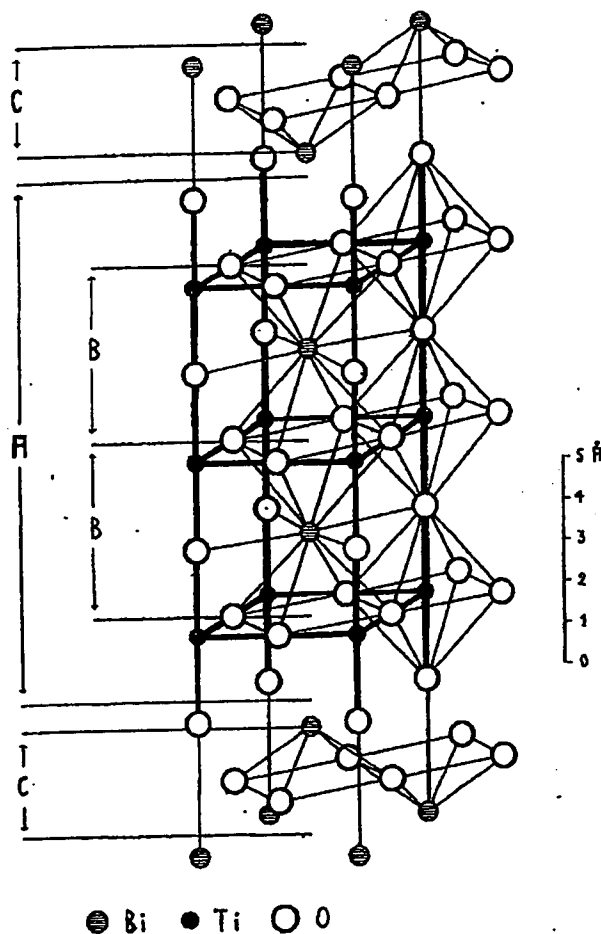
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Figure 4.

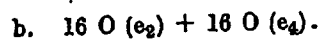
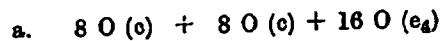
One half of the pseudo-tetragonal unit cell of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (from $z \approx 0.25$ to $z \approx 0.75$). A denotes the perovskitic layer $\text{Bi}_2\text{Ti}_2\text{O}_{10}$, C $\text{Bi}_2\text{O}_5^{2+}$ layers and B unit cells of the hypothetical perovskite structure BiTiO_3 .

In figures 3 a and 3 b sections of one fourth of the unit cell are made for $z = 0$ and $z = 0.25$. (The projections of the positions of the Bi_1 , Bi_2 and Ti atoms are denoted by: white circles, double circles and black circles respectively. The same scale is used as for figure 2). Regions where oxygen atoms might be situated are shown by shaded areas. In figure 3 a the positions of the Ti atoms are assumed to be: $00\frac{1}{2}$ and $0y\bar{z}$; $0y\bar{z}$ $y = 0.62$ $z = 0.139$ and in figure 3 b, $0y0$ $y = 0.62$ and $\pm 00z$ $z = 0.324$.

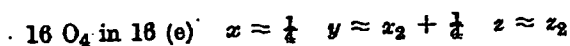
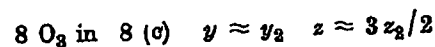
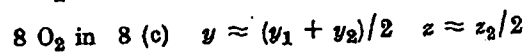
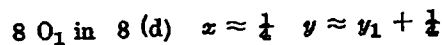
As in the discussion above it was tried to find positions for the O atoms giving an octahedral arrangement around Ti_1 and Ti_2 . Only with O atoms situated in the positions 8 (d) $x \approx \frac{1}{4}$ $y \approx y_1 + \frac{1}{4}$ and 8 (e) $y \approx y_1$ $z \approx 0.058$ would Ti_1 be surrounded by regular octahedra (see figure 3). It was therefore assumed that these positions are occupied by oxygen atoms. For oxygen atoms in contact with Ti_2 , the point positions 8 (e) and 16 (e) are possible. With 8 O situated at 8 (e), every Ti atom is in contact with one oxygen atom; with 16 O in 16 (e), Ti_2 may be in contact with 2 O (e_2) or 4 O ($y \approx y_2 + \frac{1}{4}$ $z \approx z_2$) (e_4). Bear-

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ing in mind that the unit cell contains 48 O and assuming 16 O to be situated at 8 (c) + 8 (d) (so as to form an octahedron around Ti_1), the following arrangements giving 6 O around Ti_2 seemed possible:



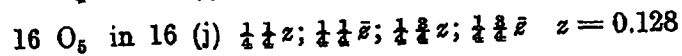
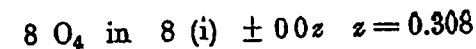
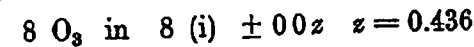
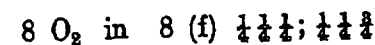
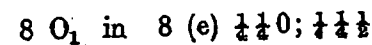
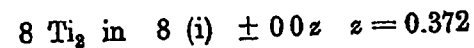
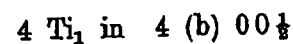
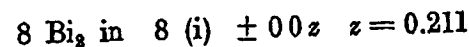
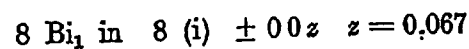
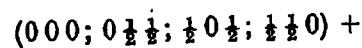
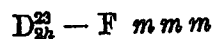
With b. no combination giving octahedra of O around Ti_2 could be found. With a., however, arrangements could be found allowing Ti_2 to be surrounded by an almost regular octahedron. The following parameters for oxygen atoms in contact with Ti_1 or Ti_2 were assumed:



For the remaining 8 O there seemed to be room only in the position 8 (b) $y \approx \frac{1}{4}$. It is seen that these positions are basically the same as were arrived at when space group D_2^7 was assumed, except for possible small shifts in the y direction.

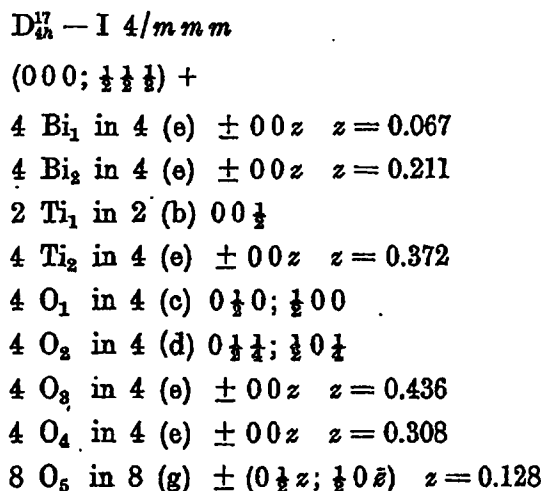
Thus no new arrangement was found by assuming C_{2h}^{18} a or b. In Table 2 (pseudo-tetragonal indices) the intensities, calculated by means of the formula $I = (10 F/4 f_{Bi})^2$, are compared with the observed ones. Since the ratios f_{Ti}/f_{Bi} and f_O/f_{Bi} vary with $\sin \theta/\lambda$ they were interpolated for every reflection from values taken from the International Tables (3). Table 2 shows good agreement between the calculated and observed intensities.

The following structure is thus proposed:



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For the pseudo-tetragonal cell the positions will be:



In figure 4 one half of the pseudo-tetragonal unit cell is pictured. The structure consists of $\text{Bi}_2\text{O}_7^{2+}$ layers alternating with $\text{Bi}_2\text{Ti}_3\text{O}_{10}^{2-}$ layers. The arrangements of the atoms within the $\text{Bi}_2\text{Ti}_3\text{O}_{10}^{2-}$ layers seems to be the same as that found for perovskite structures, and it is easily found by calculation that the geometrical properties of the Bi^{3+} , Ti^{4+} and O^{2-} ions make a perovskite structure possible. Thus the structure might be looked upon as a layer structure where perovskitic layers $\text{Bi}_2\text{Ti}_3\text{O}_{10}^{2-}$ — corresponding to a hypothetical perovskite structure BiTiO_3 — alternate with $\text{Bi}_2\text{O}_7^{2+}$ layers. With the notations given by LAGERCRANTZ and SILLÉN (5), the above structure might be denoted by X_{III} .

I wish to thank Professor L. G. SILLÉN for valuable discussions concerning this work.

Stockholms Högskola, Institute of Inorganic and Physical Chemistry, 1949.

REFERENCES. 1. Bannister, F. A. and Hey, M. H., *Miner. Mag.* 24 (1935), 49. — 2. Sillén, L. G., *Dissert. Stockholm* 1940. — 3. Internationale Tabellen zur Bestimmung von Kristallstrukturen, Berlin 1935. — 4. Wells, A. F., *Z. Krist.* 96 (1937), 451. — 5. Lagercrantz, A. and Sillén, L. G., *Arkiv f. Kemi etc.* 25 (1947), 49.

Tryckt den 10 januari 1950

Uppsala 1950. Almqvist & Wiksells Boktryckeri AB

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BRIEF ATTACHMENT X

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Date: March 1, 2005

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

FIRST SUPPLEMENTAL AMENDMENT

Sir:

In response to the Office Action dated July 28, 2004, please consider the
following:

ATTACHMENT X

ARKIV FÖR KEMI Band 2 nr 37

Communicated 24 May 1960 by ARNE WESTGREN and PERCY QUENSEL

Mixed oxides with layer lattices

III. Structure of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$

By BENGT AURIVILLIUS.

With 4 figures in the text

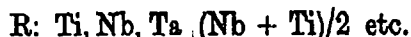
X ray studies on the compounds $\text{CaBi}_2\text{Nb}_2\text{O}_9$ (1) and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (2) have shown that the comparatively complicated chemical formulae of these compounds can be explained by simple layer structures being built up from $\text{Bi}_2\text{O}_3^{2+}$ layers and perovskite layers. The unit cells are pictured schematically in Figs. 1 a and 1 c. It was found both for $\text{CaBi}_2\text{Nb}_2\text{O}_9$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ that the symmetry was body-centered pseudo-tetragonal and that the length of the a axes had the same value (3.8 Å) while the length of the c -axis was 25 Å for $\text{CaBi}_2\text{Nb}_2\text{O}_9$ and 33 Å for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. In both structures the heavy atoms form approximately a "substructure" with a smaller body-centered tetragonal cell with $a = 3.8$ Å and $c = 25/5$ Å for $\text{CaBi}_2\text{Nb}_2\text{O}_9$ or $c = 33/7$ Å for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

The Bi_2O_2 layers and perovskite layers lie perpendicular to the c -axis. Similar layer structures have been found for a number of bismuth oxicomounds (3,4,5). The common structural element in all these compounds is quadratic Bi_2O_2 layers between which halides or certain radicals are inserted. This explains the fact that the a axes of all these compounds are of about the same length. For a survey see (5).

For the $\text{CaBi}_2\text{Nb}_2\text{O}_9$ type each perovskite layer has the composition $(\text{CaNb}_2\text{O}_7)_n$ and the height of the layer is equal to four distances Nb—O or approximately to the height of two $\text{E}2_1$ (perovskite) unit cells (see Fig. 1 a). A compound with a somewhat similar structure has previously been investigated by LAGERCRANTZ and SILLÉN (5). In this structure (see Fig. 1 b), beyerite $\text{CaBi}_2\text{O}_3(\text{CO}_3)_2$, the point positions corresponding to the positions of the Nb atoms in $\text{CaBi}_2\text{Nb}_2\text{O}_9$ are occupied by "rotating" CO_3^{2-} groups.

For the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ type the perovskite layers have the composition $(\text{Bi}_2\text{Ti}_3\text{O}_{10})_n$ and the height of the layer is equal to six distances Ti—O or approximately to the height of three $\text{E}2_1$ unit cells.

The general formula for a compound built up in a way similar to $\text{CaBi}_2\text{Nb}_2\text{O}_9$ but where the height of the perovskite layer enclosed between a pair of Me_2O_2 layers is equal to the height of m $\text{E}2_1$ cells, will be:



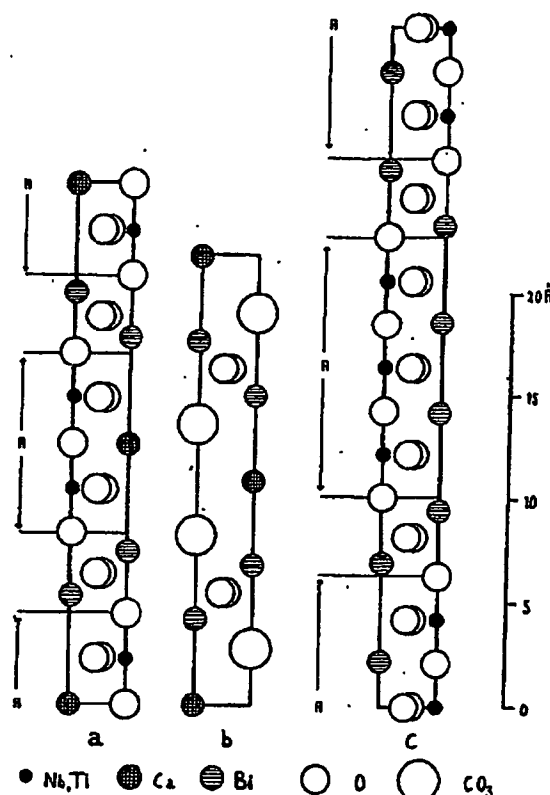
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Fig. 1. Schematic pictures of the structures of a. $\text{CaBi}_2\text{Nb}_2\text{O}_9$, b. $\text{CaBi}_2\text{O}_5(\text{CO}_3)_2$ and c. $\text{Bi}_4\text{Ti}_5\text{O}_{18}$. The vertical lines indicate the lines $00z$ and $\frac{1}{2}z$ in the unit cells. A denotes perovskitic ($E2_1$) regions in the structures.

It seemed of interest to investigate whether compounds could be synthesized with $m = 4$. The present investigation shows that structures of the above type with $m = 4$ exist.

Mixtures of Bi_2O_3 , BaCO_3 and TiO_2 , corresponding to the composition $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$, were prepared and heated to 1100°C . Single crystals, thin plates, were picked out and Weissenberg photographs were taken. These could be interpreted by means of a body-centered tetragonal cell with $a = 3.86 \text{ \AA}$ and $c = 41.7 \text{ \AA}$. The strong lines of the powder photographs (taken from preparations heated to 900°C (Au crucible) or 1100°C (Pt crucible)) were easily identified since they could all be described with the aid of the "sub-lattice" ($a = 3.86$ $c = 41.7/9$). If the c axis were 9 fold even the weak lines could be explained (Table 3). In this way the cell edges were found to be $a = 3.864 \text{ \AA}$ and $c = 41.76 \text{ \AA}$. The observed density was 7.2, which agrees fairly well with the assumption of 2 formula units/unit cell (calculated density 7.49).

The Weissenberg photographs registered $0kl$, $1kl$, hhl and $h, h+1, l$. In the Weissenberg and powder photographs there was nothing to indicate a lower Laue symmetry than $D_{4h}-4/mmm$. Except for the extinctions due to the body-centering, hkl occurring only for $h+k+l=2n$, no systematic extinctions were found, which is characteristic of the space groups C_{4v}^2 , D_{2d}^{11} and D_{4h}^{17} . Fig. 2



Fig. 2. Patterson

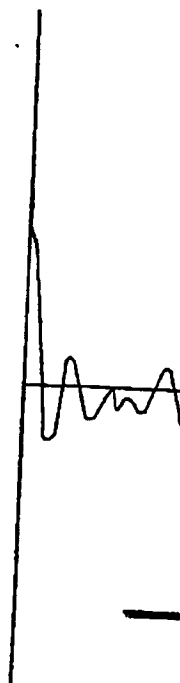


Fig. 3. Three dimensional material was used the amplitudes are The ver

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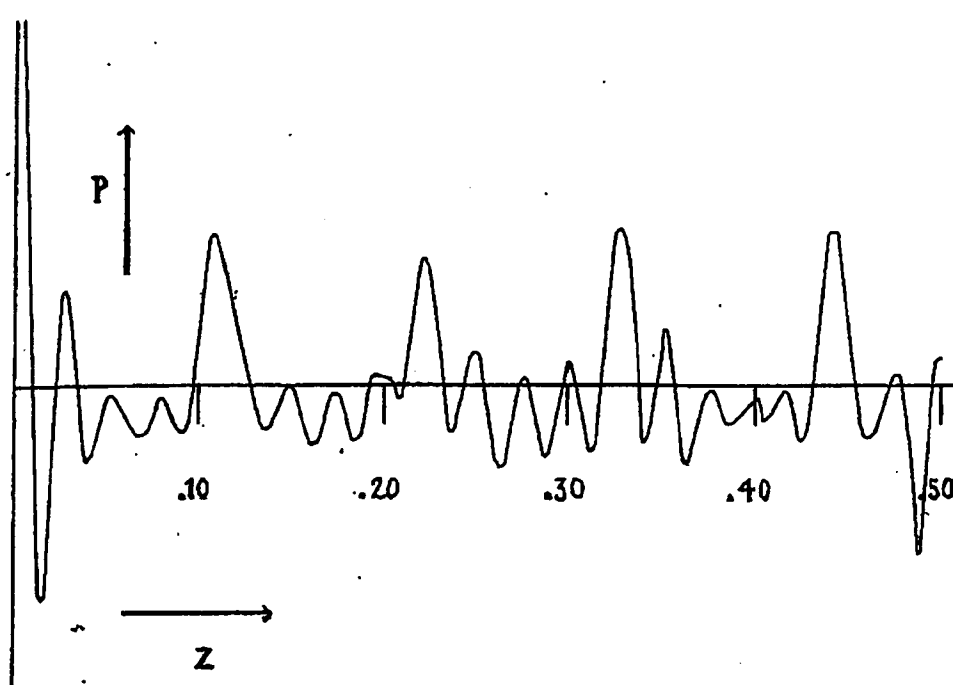


Fig. 2. Patterson Harker function of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ along $00z$. All observed reflexions were used for this calculation.

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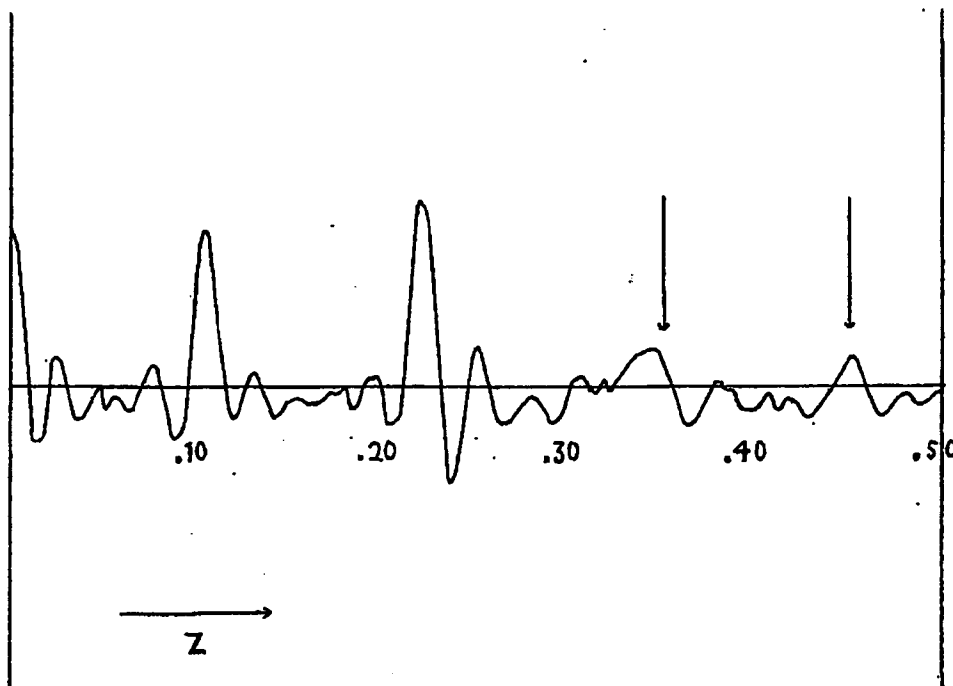


Fig. 3. Three dimensional Fourier cut along $00z$ for $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$. The same intensity material was used as for the Patterson Harker analysis pictured in Fig. 2. The signs of the amplitudes are the same as those obtained in the structure factor calculation for Table 2. The vertical arrows correspond to the z_{T1} values actually assumed.

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shows the Patterson Harker function along 00z. For all observed reflexions the F^2 values were estimated from: $F^2 \approx I_{\text{obs.}} \frac{\sin^2 \theta}{1 + \cos^2 2\theta}$. As expected large peaks appear at $z \approx 1/9, 2/9, 3/9$ and $4/9$.

It is interesting to compare the cell dimensions found above with the ones which might be expected if the compound $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ is assumed to have a structure similar to that of $\text{CaBi}_2\text{Nb}_2\text{O}_9$ but with $m = 4$. In this case the c axis would have about the same value as found. The length of the c axis might be estimated in the following way: The c axis of $\text{Bi}_2\text{NbTiO}_9$ ($m = 2$ see (1)) is 25.11 Å; the value for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($m = 3$ see (2)) is 32.83, the difference is 7.72. If twice this value is added to the c axis of $\text{BaBi}_2\text{Nb}_2\text{O}_9$ ($m = 2$) the value 41.0 Å is obtained. The value actually found was, as mentioned above, 41.76 Å.

From the composition, cell dimensions, and crystal symmetry it seemed *a priori* probable that the structure of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ was the one we anticipated. Therefore, the parameters were worked out with the aid of the parameters found for

Table 1

Weissenberg photographs of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$. Cu K_α radiation. For zero order photographs the regions of maximum absorption (see Wells (6)) are indicated by dotted lines. The intensities of 101, 103 and 105 have been taken from a zero order photograph, those of 1027–1049 from a first order photograph rotated around (100).

h	001	201	221	401	111	311	331
2		—	vw	—	—	—	vw
4		—	—	—	vw	—	vvw
6	vw	vvw	vw	—	w	—	vvw
8	m	m	w	—	m	vvw	vvw
10	m	m	w	—	st	vw	w
12	w	vvw	vw	—	vvw	—	w
14	w	—	vvw	—	w	—	—
16	st	w	m ⁺	vvw	m	vvw	m
18	vst	m	st	w	vst	w	st
20	st	w	w	vvw	w	—	—
22	m ⁺	vvw	vvw	vvw	vw	—	vw
24	w	vvw	vvw	vvw	vw	—	w
26	w	vvw	—	—	w	vvw	w
28	st	m ⁺	w ⁺	m ⁺	m	vw	—
30	w	w	w	m ⁺	—	vw	—
32	w	w ⁺	w	—	m	w	—
34	m	m	m ⁺	—	m	m	—
36	st	st	st	—	m ⁺	m	—
38	vvw	—	—	—	w	—	—
40	st	st	st	—	st	st	—
42	vvw	—	—	—	vw	—	—
44	—	—	—	—	—	—	—
46	m	m	—	—	st	—	—
48	w	m	—	—	st	—	—
50	w ⁺	—	—	—	m	—	—
52	w ⁺	—	—	—	—	—	—

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Table 1 (cont.)

Weissenberg photographs of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$. Cu K_α radiation.

h	101	211	301	321	411
1	m	w	vw	vw	—
3	vvw	vvw	—	vvw	—
5	vvw	—	—	—	—
7	w	vw	vvw	w	—
9	vst	st	m	m	w
11	—	—	—	—	—
13	w	—	—	—	—
15	w ⁺	—	vvw	—	—
17	m	vvw	vvw	—	—
19	st	vw	vvw	vvw	vvw
21	w	—	vvw	vvw	vvw
23	w	—	vvw	vvw	m
25	m ⁺	vw	vw	vw	m ⁺
27	st	m	w	m	—
29	m	vw	vvw	vvw	—
31	m	w	vw	vw	—
33	vw	vvw	vvw	vw	—
35	—	—	—	—	—
37	m ⁺	m	m	—	—
39	vw	w	m	—	—
41	w	w	w ⁺	—	—
43	w ⁺	m ⁺	—	—	—
45	m	m ⁺	—	—	—
47	—	—	—	—	—
49	st	—	—	—	—
51	—	—	—	—	—

$\text{Bi}_3\text{NbTiO}_9$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The positions of the heavy atoms might be expected to be: 2 Ba in 000, 4 Bi in $\pm 00z_1$, 4 Bi in $\pm 00z_2$.

The positions of the Ti and O atoms might be expected to be:

4 Ti in $\pm 00z_3$, 4 Ti in $\pm 00z_4$, 2 O in $00\frac{1}{2}$, 8 O in $\pm (0\frac{1}{2}(\frac{1}{2}-z_3), \frac{1}{2}0(\frac{1}{2}-z_3))$, 8 O in $\pm (0\frac{1}{2}(\frac{1}{2}-z_4), \frac{1}{2}0(\frac{1}{2}-z_4))$, 4 O in $\pm 00(z_3 + z_4)/2$, 4 O in $\pm 00(z_3 - (z_4 - z_3)/2)$, 4 O in $0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}$
 $z_1 \approx 1/9$ $z_2 \approx 2/9$ $z_3 \approx 0.350$ $z_4 \approx 0.450$

These atomic positions would give rise to high peaks in the Patterson-Harker plot at the same values as actually found. The calculated area ratios agree, however, with the observed ones only in as much as the biggest area is found for the peak at 1/9. The reasons might be an incorrect choice of the zero level and errors in the estimation of the intensities.

The parameters were varied around the above values for different positions of the Ba atoms: 2 Ba in 000, $00z_1$ or $00z_2$, 2 Ba equally distributed over $(000 + 00z_1)$, $(000 + 00z_2)$, $(00z_1 + 00z_2)$ or $(000 + 00z_1 + 00z_2)$. The best agreement seemed to be for $z_1 = 0.106 \pm 0.001$, $z_2 = 0.221 \pm 0.001$, $z_3 = 0.352 \pm 0.004$, $z_4 = 0.452 \pm 0.004$ with 2 Ba equally distributed over $(000 + 00z_1 +$

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Table 2

Weissenberg photographs of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$. Cu K_α radiation

$$I_{\text{calc.}} = (2.5 F/t_B)^2$$

l	$I_{\text{obs.}}$ 101	$I_{\text{calc.}}$ 101	$I_{\text{obs.}}$ 211	$I_{\text{calc.}}$ 211	$I_{\text{obs.}}$ 301	$I_{\text{calc.}}$ 301
1	m	73	w	90	vw	94
3	vvw	5.8	vvw	7.3	—	8.4
5	vvw	4.8	—	5.8	—	5.8
7	w	30	vw	31	vvw	32
9	vst	620	st	610	m	630
11	—	13	—	12	—	14
13	w	25	—	24	—	24
15	w ⁺	62	—	60	vvw	60
17	m	94	vvw	92	vvw	90
19	st	160	vw	170	vvw	170
21	w	15	—	12	vvw	12
23	w	19	—	18	vvw	18
25	m ⁺	120	vw	120	vw	120
27	st	320	m	320	w	320
29	m	45	vw	45	vvw	44
31	m	160	w	160	vw	160
33	vw	56	vvw	56	vvw	56
35	—	13	—	12	—	12
37	m ⁺	300	m	300	m	300
39	vw	12	w	13	m	13
41	w	15	w	14	w ⁺	15
43	w ⁺	200	m	200	—	—
45	m	180	m ⁺	180	—	—
47	—	18	—	—	—	—
49	st	250	—	—	—	—
51	—	3.6	—	—	—	—
l	$I_{\text{obs.}}$ 001	$I_{\text{calc.}}$ 001	$I_{\text{obs.}}$ 111	$I_{\text{calc.}}$ 111	$I_{\text{obs.}}$ 221	$I_{\text{calc.}}$ 221
2	—	—	—	0.5	vw	0.6
4	—	—	vw	4.8	—	5.3
6	vw	21	w	23	vw	24
8	m	110	m	100	w	110
10	m	62	st	280	w	98
12	w	12	vvw	6.3	vw	9.6
14	w	14	w	16	vvw	14
16	st	83	m	79	m ⁺	81
18	vst	440	vst	430	st	450
20	st	170	w	36	w	120
22	m ⁺	100	vw	79	vvw	92
24	w	81	vw	86	vvw	78
26	w	39	w	36	—	39
28	st	280	m	240	w	280
30	w	2.6	—	11	w	1.4
32	w	11	m	20	w	12
34	m	140	m	110	m ⁺	140
36	st	240	m ⁺	240	st	240
38	vvw	19	w	36	—	21
40	st	380	st	230	st	340
42	vvw	11	vw	22	—	—
44	—	3.2	—	4.8	—	—
46	m	240	st	230	—	—
48	w	69	st	46	—	—
50	w ⁺	53	m	110	—	—
52	w ⁺	280	—	—	—	—

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Table 3

Powder photographs of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ Cr K_α radiation.

hkl	$10^4 \sin^2 \theta_{\text{calc.}}$	$10^4 \sin^2 \theta_{\text{obs.}}$	$I_{\text{obs.}}$	hkl	$10^4 \sin^2 \theta_{\text{calc.}}$	$10^4 \sin^2 \theta_{\text{obs.}}$	$I_{\text{obs.}}$
0010	753	745	w	2018	5443	5440	vw
101	887	878	m	1025	5582	5581	w
105	1067	1058	vw	2113	5667	5669	vvw
109	1489	1481	st	0028	5900	5892	vw
110	1758	1751	m	2018	5954	5960	m
0016	1927	1915	vvw	2115	6088	6089	vw
116	2031	2018	vw	1124	6093	6089	vw
118	2240	2236	vw	1027	6365	6364	m
0018	2438	2423	m ⁻	2020	6526	6529	vw broad
1110	2511	2504	m ⁺	220	7032		
1015	2572	2567	vvw	222	7064	7070	w broad
0020	3010	2992	w	2119	7112		
1017	3054	3051	w	305	8099		
200	3516	3514	m	1031	8111	8104	vvw
1019	3596	3600	w ⁺	2214	8114		
1116	3685	3681	w	2123	8376	8365	vw
208	3998	3996	vw	2214	8507		
1118	4196	4186	m	309	8521	8520	m
1021	4198			1130	8531		
2010	4269	4265	w	310	8802		
211	4403	4402	vw	3011	8812	8802	m
213	4418			312	8820		
217	4764	4774	vw	1033	9074	9092	w broad
1120	4768			2125	9098		
2014	4991	5009	m ⁺	1132	9464	9484	w broad
219	5005			2218	9470		

00 z_2). Other distributions of Ba should, however, not be excluded; as will be seen the three dimensional Fourier cut along 00 z (see Fig. 3) seems to favour the following Me arrangement: 4 Bi \pm 00 z_2 and (2 Ba + 4 Bi) equally distributed over the positions 000 and \pm 00 z_1 .

From Table 1 it is seen that roughly for the same value of l : $I_{00l} \approx I_{20l} \approx I_{22l} \approx I_{40l}$, $I_{11l} \approx I_{31l} \approx I_{33l}$, $I_{10l} \approx I_{21l} \approx I_{30l} \approx I_{32l} \approx I_{41l}$ as might be expected from the above atomic positions with atoms only on the lines 00 z , $\frac{1}{2}$ 1 z , 0 $\frac{1}{2}$ 1 z and $\frac{1}{2}$ 0 z . Table 2 gives calculated and observed intensities for the rows 00 l , 10 l , 11 l , 21 l , 22 l and 30 l . It was found from the Weissenberg photographs that 0028 > 0030 and 1037 > 1039 (see Table 2) but the observed ratios do not seem to be as large as those calculated. This is more clearly seen for the rows 40 l and 30 l where 4028 < 4030 and 3037 > 3039. These discrepancies could neither be removed by small variations in the z parameters nor by assuming other distributions of the Ba atoms for the structure factor calculations. Other discrepancies found from Tables 1 and 2 are 222:224, 332:334, 0050:0052 and 1148:1152. However, for most reflexions the agreement is quite good and considering the errors which might be introduced by absorption effects and errors in the ratios $f_{\text{Ti}}/f_{\text{Bi}}$ and $f_{\text{O}}/f_{\text{Bi}}$ the agreement might on the whole be classified as fairly good.

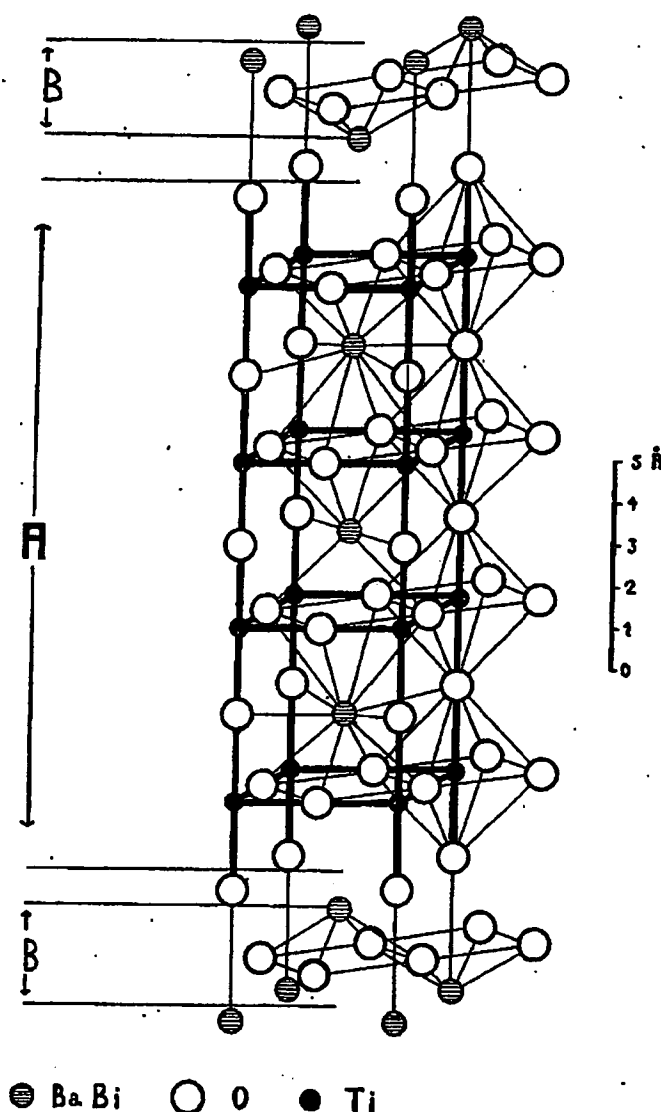
B. AURIVILLIUS, *Mixed oxides with layer lattices. III*

Fig. 4. One half of the unit cell of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$. A denotes the perovskitic region and B the Me_2O_2 layers.

The following structure is therefore proposed:
 $D_{2d}^{17} - I4/mmm$
 $(000, \frac{1}{2}\frac{1}{2}\frac{1}{2}) +$

2 Me_1 in 2 (a) 000
 2 O_1 in 2 (b) $00\frac{1}{2}$
 8 O_2 in 8 (g) $0\frac{1}{2}z; 0\frac{1}{2}\bar{z}; \frac{1}{2}0z; \frac{1}{2}0\bar{z}$ $z = 0.048$
 4 Ti_1 in 4 (e) $00z; 00\bar{z}$ $z = 0.452$
 4 O_3 in 4 (e) $z = 0.402$

Ba a1

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 $\frac{1}{2}\frac{1}{2}0;$
 $\frac{1}{2}\frac{1}{2}z;$
8 (i) z
8 Me_2

The

$\text{O}_1 - \frac{1}{2}$
 $\text{O}_2 - \frac{1}{2}$
 $\text{O}_3 - \frac{1}{2}$
 $\text{O}_4 - \frac{1}{2}$

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4 Me ₂ in 4 (e)	$z = 0.106$
8 O ₄ in 8 (g)	$z = 0.148$
4 Ti ₂ in 4 (e)	$z = 0.352$
4 O ₅ in 4 (e)	$z = 0.302$
4 Me ₃ in 4 (e)	$z = 0.221$
4 O ₆ in 4 (d) $0\frac{1}{2}\frac{1}{2}; \frac{1}{2}0\frac{1}{2}$	

Ba and Bi equally distributed over all Me positions.

If the structure is described by means of an orthorhombic space group (D_{2h}^{23}), as used for the structures of Bi₃NbTiO₉ and Bi₄Ti₃O₁₂, the positions will be: $D_{2h}^{23} - F m m m$ (000; $\frac{1}{2}\frac{1}{2}0$; $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}0\frac{1}{2}$) + 4 Me₁ in 4 (a) 000, 4 O₁ in 4 (b) $00\frac{1}{2}$, 16 O₂ in 16 (j) $\frac{1}{4}\frac{1}{4}z$; $\frac{1}{4}\frac{1}{4}\bar{z}$; $\frac{1}{4}\frac{1}{4}z$; $\frac{1}{4}\frac{1}{4}\bar{z}$; $z = 0.048$, 8 Ti₁ in 8 (i) 00z; $00\bar{z}$ $z = 0.452$, 8 O₃ in 8 (i) $z = 0.402$, 8 Me₂ in 8 (i) $z = 0.106$, 16 O₄ in 16 (j) $z = 0.148$, 8 Ti₂ in 8 (i) $z = 0.352$, 8 O₅ in 8 (i) $z = 0.302$, 8 Me₃ in 8 (i) $z = 0.221$, 8 O₆ in 8 (f) $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; $\frac{1}{4}\frac{1}{4}\frac{3}{4}$.

The distances (Å) and coordination will be:

O ₁ —8 O ₂ = 2.78	O ₂ —4 O ₃ = 2.73	Me ₂ —4 O ₃ = 3.10	Ti ₁ —O ₃ = 2.09
O ₃ —4 O ₃ = 2.84	O ₄ —4 O ₄ = 2.73	Me ₂ —4 O ₃ = 2.75	Ti ₁ —4 O ₂ = 1.93
O ₃ —4 O ₄ = 2.84	O ₅ —4 O ₆ = 2.73	Me ₂ —4 O ₄ = 2.61	Ti ₁ —O ₁ = 2.00
O ₅ —4 O ₆ = 2.91			
	Me ₁ —8 O ₂ = 2.78	Me ₃ —4 O ₆ = 2.28	Ti ₂ —O ₃ = 2.09
	Me ₁ —4 O ₁ = 2.73	Me ₃ —4 O ₅ = 2.89	Ti ₂ —4 O ₄ = 1.93
		(Me ₃ —4 O ₄ = 3.64)	Ti ₂ —O ₅ = 2.09

One half of the unit cell is shown in Fig. 4.

I wish to thank Professor L. G. SILLÉN for valuable discussions on this work.

Stockholms Högskola, Institute of Inorganic and Physical Chemistry. May 1950.

REFERENCES. 1. Aurivillius, B., Arkiv Kemi 1 (1950) 463. — 2. —, Ibid, 1 (1950) 499. — 3. Bannister, F. A. and Hey, M. H., Miner. Mag. 24. (1935) 49. — 4. Sillén, L. G., Dissert., Stockholm 1940. — 5. Lagercrantz, A. and Sillén, L. G., Arkiv Kemi 25 No 20, 1948. — 6. Wells, A. F., Z. Krist. 96 (1937) 451.

Tryckt den 14 oktober 1950

Uppsala 1950. Almqvist & Wiksells Boktryckeri AB

BRIEF ATTACHMENT Y

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Date: March 1, 2005

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

FIRST SUPPLEMENTAL AMENDMENT

Sir:

In response to the Office Action dated July 28, 2004, please consider the
following:

ATTACHMENT Y

ARKIV FÖR KEMI Band 5 nr 4

Communicated 14 May 1952 by ARNE WESTEREN

The structure of $\text{Bi}_2\text{NbO}_5\text{F}$ and isomorphous compounds

By BENGT AURIVILLIUS

With 1 figure in the text

X-ray studies made previously on the compounds $\text{CaBi}_2\text{Nb}_2\text{O}_9$, $\text{Bi}_4\text{Ti}_3\text{O}_{13}$ and $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ (1) showed that they have very similar structures. The symmetry is tetragonal or pseudotetragonal, and the structures are each built up of quadratic Bi_2O_3 layers alternating with perovskite layers, the latter having different heights in the three different cases. The generalized formula for the compounds might be written $\text{Me}_2\text{O}_3 (\text{Me}'_{m-1} \text{R}_m \text{O}_{8m+1})$ where Me' is the 12 coordinated metal atom in the perovskite layers and R the 6 coordinated atom. The formulae for the above compounds, $\text{Bi}_2\text{O}_3(\text{CaNb}_2\text{O}_7)$, $\text{Bi}_2\text{O}_3(\text{Bi}_2\text{Ti}_3\text{O}_{10})$ and $\text{Bi}_2\text{O}_3[(\text{BaBi}_2)\text{Ti}_4\text{O}_{13}]$ thus have m values of 2, 3 and 4. The simplest case, $m=1$, would correspond to the formula $\text{Me}_2\text{O}_3(\text{RO}_4)$ and to a structure built up of Me_2O_3 layers and layers of RO_4 octahedra each octahedron sharing four corners. Compounds of this type have, however, not been successfully synthesized as yet.

The present paper deals with the compounds $\text{Bi}_2\text{NbO}_5\text{F}$, $\text{Bi}_2\text{TaO}_5\text{F}$ and $\text{Bi}_2\text{TiO}_4\text{F}_2$, which correspond to the simplest case, $m=1$ above, except that some of the O atoms are replaced by F atoms. The formulae of the compounds might thus be written: $\text{Bi}_2(\text{O}, \text{F})_2\text{Nb}(\text{O}, \text{F})_4$ etc.

Preparation, powder photographs and analyses

$\text{Bi}_2\text{NbO}_5\text{F}$: When a mixture of BiF_3 and Nb_2O_5 in the mol ratio 4:1 was heated in air at 800°C for a short time, a few single crystals (very thin plates) were obtained. Powder photographs of this sample indicated a tetragonal unit cell with the same cell dimensions as would be expected for the above general type when $m=1$. The best conditions for the formation of this phase were then studied by heating 2.5 g mixtures ($2\text{BiF}_3 + \frac{1}{2}\text{Nb}_2\text{O}_5$) in air at 640°C , this low temperature being chosen to reduce the volatility of the BiF_3 . The reaction times were varied from 5–40 hours, and powder photographs were taken of each product. For reaction times of 7–15 hours the lines of the above tetragonal phase predominated in the powder photographs, the few extra lines were very weak (see Table 1).

The fluorine content was found to vary from 4.0 % (7 hours) to 2.4 % (15 hours), whereas the calculated value for $\text{Bi}_2\text{NbO}_5\text{F}$ is 3.2 %. No variation in the size of the cell with the fluorine content was found, and it therefore seems probable that the composition of the phase is constant and that the observed variation in the F content is due to the presence of small impurities which are not visible in the powder photo-

B. AURIVILLIUS, *The structure of $\text{Bi}_2\text{NbO}_5\text{F}$ and isomorphous compounds*

Table 1

Powder photographs of $\text{Bi}_2\text{NbO}_5\text{F}$ (sample with 2.8 % F)
Or K radiation $\lambda_{\text{Or K}} = 2.2909 \text{ \AA}$

hkl	$10^4 \cdot \sin^2 \theta_{\text{calc}}$	$10^4 \cdot \sin^2 \theta_{\text{obs}}$	I_{obs}
103	1319	1332	st
006	1708	1711	m
110	1784	1795	m
112	1974	1989	vw
105	2078	2083	vw
114	2543	2547	m
—	—	2785	vw
008	3036	3033	w
—	—	3093	vw
116	3492	3490	st
200	3568	3567	st
202	3758	3754	vw
—	—	3808	vw
{109	4734 }	4737	st
{00 10	4743 }	—	—
118	4820	4827	w
213	4888	4891	st
206	5276	5292	m
215	5647	5658	w
11 10	6527	6529	vw
10 11	6631	6630	w
00 12	6830	6841	w
220	7137	7139	w
222	7327	7330	vw
301	8076	8080	vw
{219	8303 }	8304	st
{20 10	8311 }	—	—
303	8456	8456	m
11 12	8614	8611	m
226	8845	8844	m
{10 13	8908 }	8919	m
{310	8921 }	—	—
312	9111	9119	vw
305	9215	9195	vw
00 14	9297	9292	vw

Fig. 1. C

Bi_2TiO_5
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phase are
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variation
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fluorine a
of $\text{Bi}_2\text{NbO}_5\text{F}$
 $\text{Bi}_2\text{TiO}_5\text{F}_2$

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graphs. To check that the Bi/Nb ratio had not changed essentially during the heating, a complete analysis was made on one sample (9 hours heating). The following values were obtained as the mean of three analyses: Bi: $68.0 \pm 0.6\%$, Nb: $14.2 \pm 0.6\%$, F: $3.7 \pm 0.2\%$.

The values calculated for $\text{Bi}_2\text{NbO}_5\text{F}$ are:

Bi: 68.5, Nb: 15.2%, F: 3.2%.

From these figures it seems probable that the formula of the compound is $\text{Bi}_2\text{NbO}_5\text{F}$.

$\text{Bi}_2\text{TaO}_5\text{F}$ was prepared in exactly the same way as $\text{Bi}_2\text{NbO}_5\text{F}$. No analysis was made since the powder photographs were similar to those of $\text{Bi}_2\text{NbO}_5\text{F}$ and niobium and tantalum compounds are usually isomorphous.

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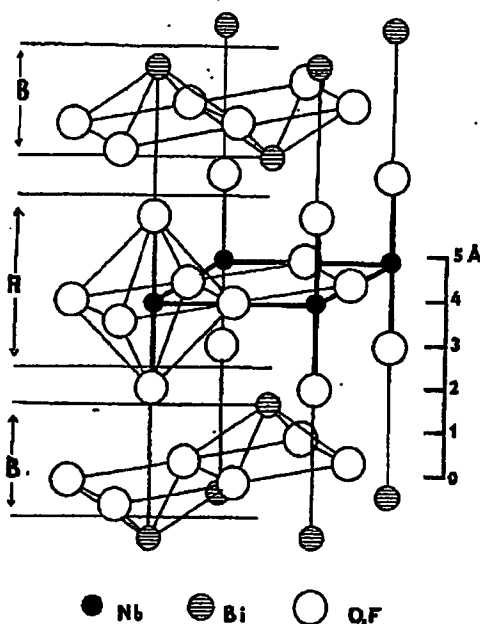


Fig. 1. One half of the unit cell of $\text{Bi}_2\text{NbO}_6\text{F}$. A denotes the region of $\text{Nb}(\text{O},\text{F})_6$ octahedra and B the $\text{Bi}_2(\text{O},\text{F})_8$ layers.

$\text{Bi}_2\text{TiO}_4\text{F}_2$: Mixtures of bismuth fluoride and titanium oxide in the mol ratio 2:1 (total 2.3 g) were heated in air at 640° for various lengths of time. The powder photographs obtained from samples heated for 3 or 5 hours could be interpreted by assuming a mixture of BiOF (2) and a phase whose cell dimensions were nearly the same as those of $\text{Bi}_2\text{NbO}_6\text{F}$. (See Table 2, where the reflexions from the BiOF phase are designated by b and those from the other phase by a). The fluorine contents of the mixed samples were found to be 6.4 % (5 hours) and 8.4 % (3 hours) but no variation of the cell size with the fluorine content was found. The calculated values are 7.8 % for BiOF and 6.7 % for $\text{Bi}_2\text{TiO}_4\text{F}_2$. From the original Bi/Ti ratio, from the fluorine analysis and from the similarity of the powder photographs with those of $\text{Bi}_2\text{NbO}_6\text{F}$ (Tables 1 and 2), it was concluded that the formula of the phase is $\text{Bi}_2\text{TiO}_4\text{F}_2$.

Methods of analysis: Fluorine. The samples were first decomposed by fusing with NaOH , and were then distilled with HClO_4 as described by WILLARD and WINTER (3). The distillate was titrated with $\text{Th}(\text{NO}_3)_4$ using Na-alizarinsulphonate as indicator.

Bismuth and Niobium. The samples were brought into solution, and niobium was determined as described in Scott's "Standard Methods" (4). Bismuth was first precipitated as Bi_2S_3 , which was then redissolved, converted to Bi_2O_3 and weighed as such.

Unit cells and space group

The dimensions of the unit cells were determined from powder photographs taken with focusing cameras of the Phragmén type (Tables 1 and 2). The radiation used

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Table 2

Powder photographs of $\text{Bi}_2\text{TiO}_4\text{F}_2$ (mixed with BiOF) Cr K radiation ($\lambda_{\text{Cr K}_\alpha} = 2.2909 \text{ \AA}$). a denotes the $\text{Bi}_2\text{TiO}_4\text{F}_2$ phase and b the BiOF phase

hkl	phase	$10^4 \sin^2 \theta_{\text{calc}}$	$10^4 \sin^2 \theta_{\text{obs}}$	I_{obs}
101	a	957	941	vw
101	b	1270	1265	m
{103	a	1351}		
{002	b	1352}	1354	st
006	a	1771	1767	m
110	a	1816	1811	m
110	b	1864	1858	vw
112	a	2013	1999	w
105	a	2138	2132	w+
102	b	2284	2288	vw
114	a	2603	2601	m
-	-	-	3074	vw
112	b	3216	3231	w
107	a	3319	3320	vw
116	a	3587	3600	st
200	a	3631	3624	st
200	b	3728	3744	w
202	a	3828	3822	w
103	b	3974	3982	w
-	-	-	4352	vw
204	a	4418	4426	vw
211	a	4538	4590	w
-	-	-	4674	vw
{109	a	4893}		
{113	b	4906}	4904	st
{00 10	a	4919}		
213	a	4982	4979	st
202	b	5080	5084	w
{206	a	5402}		
{004	b	5408}	5416	m+
215	a	5769	5788	m
212	b	6012	6025	m
104	b	6340	6353	w
{203	b	6770}		
{208	a	6779}	6786	m
10 11	a	6860	6869	m
217	a	6950	6950	vw
00 12	a	7084	7075	m
{220	a	7262}		
{114	b	7272}	7262	m
{220	b	7455}		
{222	a	7459}	7456	w
213	b	7702	7709	m
-	-	-	8049	vw
301	a	8210	8210	vw
-	-	-	8352	vw
{219	a	8524}		
{20 10	a	8550}	8524	st
303	a	8613	8603	m
301	b	8736	8725	w
222	b	8814	8807	w
11 12	a	8900	8900	m

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Table 2 (continued)

hkl	phase	$10^4 \sin^2 \theta_{\text{calc}}$	$10^4 \sin^2 \theta_{\text{obs}}$	I_{obs}
2 2 6	<i>a</i>	9033	9027	m
3 1 0	<i>a</i>	9078	9072	w
2 0 4	<i>b</i>	9136	9136	vw
3 1 2	<i>a</i>	9275	9272	m
3 1 0	<i>b</i>	9319	9319	w
{ 1 0 5	<i>b</i>	9382 }	9384	m
{ 3 0 5	<i>a</i>	9400 }		

was $Cr K$ ($\lambda_{Cr K_\alpha} = 2.2909 \text{ \AA}$). As mentioned above the powder photographs could be interpreted by assuming tetragonal unit cells; the cell dimensions are given below.

	a (Å)	c (Å)
$\text{Bi}_2\text{NbO}_5\text{F}$	3.835	16.63
$\text{Bi}_2\text{TaO}_5\text{F}$	3.829	16.64
$\text{Bi}_2\text{TiO}_4\text{F}_2$	3.802	16.33

The errors in these figures are estimated to be $\pm 0.1 \%$.

The observed density was 8.0 for $\text{Bi}_2\text{NbO}_5\text{F}$ (preparation with 2.8% F), which agrees fairly well with the assumption of 2 formula units per unit cell, giving a calculated density of 8.26.

Zero and first order Weissenberg photographs around the a axis were taken. There was nothing in the Weissenberg photographs to indicate a Laue symmetry lower than $D_{4h}-4/mmm$. The only extinctions found were that h, k, l were absent for $h+k+l$ odd, which is characteristic of the space groups C_{4v}^9 , D_{2d}^9 , D_{2d}^{11} and D_{4h}^{11} .

Powder photographs only were taken of the compounds $\text{Bi}_2\text{TaO}_5\text{F}$ and $\text{Bi}_2\text{TiO}_4\text{F}_2$, and from these it was concluded that these substances are isomorphous with $\text{Bi}_2\text{NbO}_5\text{F}$.

Positions of the metal atoms

$\text{Bi}_2\text{NbO}_5\text{F}$: With 2 formula units per unit cell there are 4 Bi and 2 Nb atoms per unit cell. The intensities of the spots in the Weissenberg photographs seemed in the main to depend only on the l values. Thus for l even $I_{00l} \approx I_{11l} \approx I_{20l}$ etc. and for l odd: $I_{10l} \approx I_{21l} \approx I_{30l}$ etc. With these intensity values a good approximation of the Patterson-Harker function along $00z$ could be obtained by using only the intensity values of $h0l$ and $h1l$. The Patterson-Harker function thus calculated (not given here) showed only one, big, maximum, at $z=0.34$. This maximum, and the absence of others, could be explained only by assuming that 4 Bi atoms are situated at the positions $\pm 00z$ with $z=0.17$ or $z=0.33$, and the Nb atoms at the positions $00\frac{1}{2}$ or 000 . Arbitrarily choosing 000 as the position for Nb, trial and error calculations gave the value 0.325 for the Bi parameter.

No determination of z_{Bi} was made for $\text{Bi}_2\text{TaO}_5\text{F}$.

For $\text{Bi}_2\text{TiO}_4\text{F}_2$ the powder photograph data were used to determine the Bi parameter. Assuming the Ti atoms to be situated at 000 and the O and the F atoms to occupy the same positions as given below for $\text{Bi}_2\text{NbO}_5\text{F}$, the value $z_{\text{Bi}} = 0.327 \pm 0.006$ was obtained from trial and error calculations.

B. AURIVILLIUS, *The structure of $\text{Bi}_2\text{NbO}_5\text{F}$ and isomorphous compounds*Table 3
Weissenberg photographs of $\text{Bi}_2\text{NbO}_5\text{F}$

Zero layer

<i>l</i>	<i>h k</i>		0 0		2 0		4 0		<i>l</i>
			<i>I</i> _{calc}	<i>I</i> _{obs}	<i>I</i> _{calc}	<i>I</i> _{obs}	<i>I</i> _{calc}	<i>I</i> _{obs}	
0			—	—	170	vst	37	w	0
2			—	—	10	w	3	vw	2
4			0.3	—	0.04	—	0.05	—	4
6			220	vst	67	w	34	vw	6
8			12	w	5	vw	6	vvw	8
10			3	vw	2	—	2	—	10
12			44	st	26	w	86	st	12
14			15	m	11	w			14
16			10	w	10	w			16
18			16	m	28	m			18
20			22	m					20

<i>l</i>	<i>h k</i>		1 0		3 0		<i>l</i>
			<i>I</i> _{calc}	<i>I</i> _{obs}	<i>I</i> _{calc}	<i>I</i> _{obs}	
1			7	w	1	vw	1
3			270	vst	42	w	3
5			40	w	8	vw	5
7			1	—	0.2	—	7
9			75	m	30	vw	9
11			18	w	10	vw	11
13			3	vw	3	vw	13
15			20	m	19	m	15
17			12	w			17
19			14	w			19

Positions of the O and the F atoms

The positions of the O and the F atoms could not be distinguished either from the diffraction data, or from space considerations because of the similarity in the reflecting power and ionic radii of O^{2-} and F^- . The problem is therefore treated as though O and F were the same atomic species. In the following, the O and the F atoms are denoted by (O, F) and the discussion relates to $\text{Bi}_2\text{NbO}_5\text{F}$ for which z_{Bi} could be accurately determined from the Weissenberg photographs.

It seemed reasonable to assume that the Nb atoms are surrounded by a regular or nearly regular octahedron of (O, F) atoms with distances $\text{Nb}-(\text{O}, \text{F}) \approx 2.0 \text{ \AA}$. Neglecting the polar space group C_{4v}^9 , these conditions are fulfilled only if 4 (O, F) atoms, here called (O, F)₁, are situated at the positions $\pm 00z$ with $z \approx 0.12$, and 4 (O, F) atoms, (O, F)₂, at the positions $0\frac{1}{2}0, \frac{1}{2}00$. Assuming the distance (O, F)–(O, F) to be $\geq 2.5 \text{ \AA}$ and the distance $\text{Bi}-(\text{O}, \text{F})$ to be $\geq 2.2 \text{ \AA}$ there is only room for the remaining 4 (O, F) atoms, (O, F)₃, at the positions $0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}$.

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Tabl
photographs of BiNbO_5F $\text{Cu K}\alpha$ radiation

First layer

40		l	hk	11	31				
Icalc	Iobs			Icalc	Iobs	Icalc	Iobs		
37	w	0		210	vst	36	w		
3	vw	2		17	w	4	vvw		
0.05	—	4		11	w	2	—		
34	vw	6		110	m	33	w		
6	vvw	8		27	vw	9	vw		
.....									
2	—	10		2	vvw	1	—		
		12		21	m	20	w		
86	st	14		14	w	20	w		
		16		5	w	17	w		
		18		19	m				
		20		58	st				
		l	hk	01	21	41			
				Icalc	Iobs	Icalc	Iobs	Icalc	Iobs
		1		7	—	2	vw	1	vvw
		3		270	vst	74	m	33	w
		5		40	m	13	w	7	—
		7		1	—	0.3	—	0.2	—
.....									
		9		75	vst	40	w	53	w
		11		18	m	12	vvw	51	w
.....									
		13		3	vw	3	vw		
		15		20	m	19	m		
		17		12	w	19	m		
		19		14	w				

The coordination and distances in Å will be:

$$\begin{array}{ll}
 \text{Bi}-4 (\text{O}, \text{F})_3 = 2.29 & \text{Nb}-2 (\text{O}, \text{F})_1 = 2.0 \\
 \text{Bi}-4 (\text{O}, \text{F})_1 = 2.9 & \text{Nb}-4 (\text{O}, \text{F})_2 = 1.92 \\
 (\text{O}, \text{F})_3-4 (\text{O}, \text{F})_3 = 2.71 & (\text{O}, \text{F})_2-4 (\text{O}, \text{F})_2 = 2.71 \\
 (\text{O}, \text{F})_1-4 (\text{O}, \text{F})_3 = 2.9 & (\text{O}, \text{F})_1-4 (\text{O}, \text{F})_2 = 2.8
 \end{array}$$

The proposed structure is given in the summary. Calculated and observed intensities for the reflexions in the Weissenberg photographs are given in Table 3. I_{calc} is derived as follows:

$$I_{\text{calc}} = \frac{1 + \cos^2 2\theta}{1600 \cdot \sin 2\theta} \cdot F^2 \text{ where } F = \sum f \cos 2\pi(hx + ky + lz).$$

The lines of maximum absorption in the Weissenberg photographs (see 5) are indicated by dotted lines in Table 3. If the absorption effects are taken into account, the agreement between calculated and observed intensities is quite good.

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B. AURIVILLIUS, *The structure of $\text{Bi}_2\text{NbO}_6\text{F}$ and isomorphous compounds*

Discussion of the structure

Even if the $(\text{O}, \text{F})_1$ atoms (see above) are assumed to occupy such a position that the distance $\text{Bi}-4(\text{O}, \text{F})_1$ is as small as possible [$z(\text{O}, \text{F})_1 = 0.15$, $(\text{O}, \text{F})_1 = (\text{O}, \text{F})_2 = 2.5$, $\text{Nb}-2(\text{O}, \text{F})_1 = 2.5$, $\text{Bi}-4(\text{O}, \text{F})_1 = 2.7$], the distance $\text{Bi}-4(\text{O}, \text{F})_1$ will still be much longer than the distance $\text{Bi}-4(\text{O}, \text{F})_3$. It therefore seems appropriate to describe the structure of $\text{Bi}_2\text{NbO}_6\text{F}$ as being built up of $\text{Bi}_2(\text{O}, \text{F})_2$ layers alternating with octahedral layers having the composition $\text{Nb}(\text{O}, \text{F})_4$, both layers being perpendicular to the c -axis. It might be pointed out that the structure of $\text{Bi}_2(\text{O}, \text{F})_2\text{Nb}(\text{O}, \text{F})_4$ is basically of the same type as the " X_1 structures", $\text{Me}_2\text{O}_2\text{X}$, previously investigated by SILLÉN (6). Thus the octahedral sheets $\text{Nb}(\text{O}, \text{F})_4$ correspond to single layers of halogen atoms, X , in $\text{Me}_2\text{O}_2\text{X}$.

Discussion of the distribution of the O and the F atoms

As seen above, the distance $\text{Bi}-4(\text{O}, \text{F})_3$ is 2.29 \AA for $\text{Bi}_2\text{NbO}_6\text{F}$. For $\text{Bi}_2\text{TiO}_6\text{F}$, the corresponding distance is calculated to be $2.26 \pm 0.06 \text{ \AA}$. These distances are very nearly the same as the corresponding distances, $\text{Bi}-4 \text{ O}$, within the Bi_2O_2 layers of other bismuth oxide compounds (6). This need not, however, necessarily mean that the $\text{Bi}_2(\text{O}, \text{F})_2$ layers (see the figure) are free from F atoms, since compounds with $\text{Bi}_2(\text{O}, \text{F})_2$ layers which certainly contain F atoms have not been investigated hitherto, and thus the distances within such layers are unknown.

For the present it seems therefore best to make no special assumptions as to the distribution of the O and F atoms.

SUMMARY

The crystal structure of $\text{Bi}_2\text{NbO}_6\text{F}$ has been investigated by means of Weissenberg and powder photographs. From powder photographs the compounds $\text{Bi}_2\text{TaO}_6\text{F}$ and $\text{Bi}_2\text{TiO}_6\text{F}$ have been found to be isomorphous with $\text{Bi}_2\text{NbO}_6\text{F}$. The following structure is proposed for $\text{Bi}_2\text{NbO}_6\text{F}$:

$D_{4h}^{17} - I 4/mmm$		
$(000, \frac{1}{2}, \frac{1}{2}) +$		
2 Nb in 2 (a) :	000	
4 Bi in 4 (e) :	$\pm 00z$	$z = 0.325 \pm 0.001$
4 (O, F) ₁ in 4 (c) :	$0\frac{1}{2}0, \frac{1}{2}00$	
4 (O, F) ₂ in 4 (e) :	$\pm 00z$	$z = 0.12 \pm 0.01$
4 (O, F) ₃ in 4 (d) :	$0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}$	

The cell dimensions are $a = 3.835 \text{ \AA}$, $c = 16.63 \text{ \AA}$ for $\text{Bi}_2\text{NbO}_6\text{F}$. The positions of the metal atoms were determined from the diffraction data, those of the (O, F) atoms from space considerations. Although it does not seem improbable that O atoms alone occupy the positions $0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}$, Bi and O thus forming Bi_2O_2 layers as in other bismuth oxide compounds, nothing can be definitely stated as to the distribution of the O and F atoms.

The structure is built up of quadratic $\text{Bi}_2(\text{O}, \text{F})_2$ layers alternating with octahedral sheets having the composition $\text{Nb}(\text{O}, \text{F})_4$ (see figure) and the formula might thus be written: $\text{Bi}_2(\text{O}, \text{F})_2\text{Nb}(\text{O}, \text{F})_4$. The structure is formally related to a series of

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previously investigated structures of general formula $Me_2O_2 (Me'_{m-1}R_mO_{3m+1})$ and represents the simplest case of this series, i.e. $m=1$.

University of Stockholm, Institute of Inorganic and Physical Chemistry, May 1952.

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REFERENCES. 1. Aurivillius, B., Arkiv Kemi 2 (1950) 519. — 2. —, Arkiv Kemi Mineral. Geol., 26 B (1948) no 2. — 3. Willard, H. H. and Winter, O. B., Ind. Eng. Chem. Anal. Ed. 5 (1933) 7. — 4. Standard Methods of Chemical Analysis by W. W. Scott, fifth edition, edited by N. H. Furman, New York 1925, p. 335 and p. 338. — 5. Wells, A. F., Z. Krist. 96 (1937) 451. — 6. Sillén, L. G., Dissert. Stockholm 1940.

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BRIEF ATTACHMENT Z

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Date: March 1, 2005

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

FIRST SUPPLEMENTAL AMENDMENT

Sir:

In response to the Office Action dated July 28, 2004, please consider the
following:

ATTACHMENT Z



Superconductivity

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Horacio A. Farach

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University of South Carolina
Columbia, South Carolina



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Perovskite and Cuprate Crystallographic Structures

I. INTRODUCTION

Chapter 3 shows that the majority of single-element crystals have highly symmetrical structures, generally fcc or bcc, in which their physical properties are the same along the three crystallographic directions x , y , and z . The NaCl-type and A15 compounds are also cubic. Some compounds do have lower symmetries, showing that superconductivity is compatible with many different types of crystallographic structure, but higher symmetries are certainly more common. In this chapter we will describe the structures of the high-temperature superconductors, almost all of which are tetragonal or orthorhombic.

In Chapter 3, we also gave some examples of the role played by structure in determining the properties of superconductors. The highest transition tempera-

tures in alloys of transition metals are at the boundaries of instability between the bcc and hcp forms. The NaCl-type compounds have ordered vacancies on one or another lattice site. The magnetic and superconducting properties of the Chevrel phases depend on whether the large magnetic cations (i.e., positive ions) occupy eightfold sites surrounded by chalcogenide ions or whether the small magnetic ions occupy octahedral sites surrounded by Mo ions.

The structures described here are held together by electrons that form ionic or covalent bonds between the atoms. No account is taken of the conduction electrons, which are delocalized over the copper oxide planes and form Cooper pairs responsible for the superconducting properties below T_c . The following chapter will be devoted to explaining the role of these

conduction electrons within the frameworks of the Hubbard model and band theory. Whereas the present chapter describes atom positions in coordinate space, the following chapter relies on a reciprocal lattice elucidation of these same materials.

We begin with a description of perovskite and explain some reasons that perovskite undergoes various types of distortions. This prototype exhibits a number of characteristics that are common to the high-temperature superconducting cuprates (see Section V). We will emphasize the structural commonalities of these materials and make frequent comparisons between them. Our earlier work (Poole *et al.*, 1988) and the comprehensive review by Yvon and François (1989) may be consulted for more structural detail on the atom positions, interatomic spacings, site

and thallium high temperature superconductors (Medvedeva *et al.*, 1993).

We assume that all samples are well made and safely stored. Humidity can affect composition, and Garland (1988) found that storage of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in 98% humidity exponentially decreased the diamagnetic susceptibility with a time constant of 22 days.

II. PEROVSKITES

Much has been written about the high-temperature superconductors being perovskite types, so we will begin by describing the structure of perovskites. The prototype compound barium titanate, BaTiO_3 , exists in three crystallographic forms with the following lattice constants and unit cell volumes (Wyckoff, 1964):

cubic:	$a = b = c = 4.0118 \text{ \AA}$	$V = 64.57 \text{ \AA}^3$	(7.1)
tetragonal:	$a = b = 3.9947, c = 4.0336$	$V = 64.37 \text{ \AA}^3$	
orthorhombic:	$a = 4.009\sqrt{2} \text{ \AA}, b = 4.018\sqrt{2} \text{ \AA}, c = 3.990 \text{ \AA}$	$V = 2(64.26) \text{ \AA}^3$	

symmetries, etc., of these compounds. There have been reports of superconductivity in certain other cuprate structures (e.g., Murphy *et al.*, 1987), but these will not be reported on in this chapter.

There is a related series of layered compounds $\text{Bi}_2\text{O}_2(M_{m-1}R_m\text{O}_{3m+1})$ called Aurivillius (1950, 1951, 1952) phases, with the 12-coordinated $M = \text{Ca}, \text{Sr}, \text{Ba}, \text{Bi}, \text{Pb}, \text{Cd}, \text{La}, \text{Sm}, \text{Sc}, \text{etc.}$, and the 6-coordinated transition metal $R = \text{Nb}, \text{Ti}, \text{Ta}, \text{W}, \text{Fe}, \text{etc.}$ The $m = 1$ compound Bi_2NbO_6 belongs to the same tetragonal space group $I4/mmm, D_{4h}^{17}$ as the lanthanum, bismuth,

For all three cases the crystallographic axes are mutually perpendicular. We will comment on each case in turn.

A. Cubic Form

Above 201°C barium titanate is cubic and the unit cell contains one formula unit BaTiO_3 with a titanium atom on each apex, a barium atom in the body center, and an oxygen atom on the center of each edge of the cube, as illustrated in Fig. 7.1. This corresponds to the barium atom, titanium atom, and three oxygen atoms being placed in positions with the following x, y , and z coordinates:

E site: Ti	$(0, 0, 0)$	Ti on apex	(7.2)
F site: O	$(0, 0, \frac{1}{2}); (0, \frac{1}{2}, 0); (\frac{1}{2}, 0, 0)$	three oxygens centered on edges	
C site: Ba	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	Ba in center.	

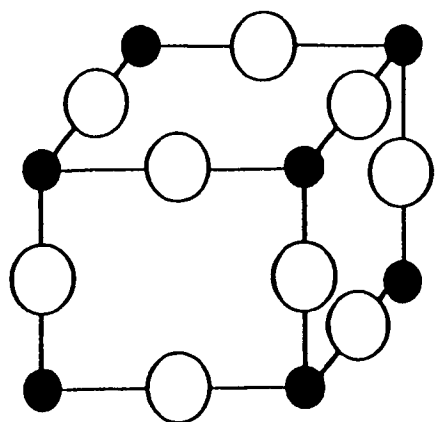


Figure 7.1 Barium titanate (BaTiO_3) perovskite cubic unit cell showing titanium (small black circles) at the vertices and oxygen (large white circles) at the edge-centered positions. Ba, not shown, is at the body center position (Poole *et al.*, 1988, p. 73).

The barium in the center has 12 nearest-neighbor oxygens, so we say that it is 12-fold coordinated, while the titanium on each apex has 6-fold (octahedral) coordination with the oxygens, as may be seen from the figure. (The notation *E* for edge, *F* for face, and *C* for center is adopted for reasons that will become clear in the discussion which follows.) Throughout this chapter we will assume that the *z*-axis is oriented vertically, so that the *x* and *y* axes lie in the horizontal plane.

Ordinarily, solid-state physics texts place the origin (0,0,0) of the perovskite unit cell at the barium site, with titanium in the center and the oxygens at the centers of the cube faces. Our choice of origin facilitates comparison with the structures of the oxide superconductors.

This structure is best understood in terms of the sizes of the atoms involved. The ionic radii of O^{2-} (1.32 Å) and Ba^{2+} (1.34 Å) are almost the same, as indicated in Table 7.1, and together they form a perfect fcc lattice with the smaller Ti^{4+} ions (0.68 Å) located in octahedral holes surrounded entirely by oxygens. The octahedral holes of a close-packed oxygen lattice have a radius of 0.545 Å; if these holes were empty the lattice constant would be $a = 3.73$ Å, as noted in Fig. 7.2a. Each

titanium pushes the surrounding oxygens outward, as shown in Fig. 7.2b, thereby increasing the lattice constant. When the titanium is replaced by a larger atom, the lattice constant expands further, as indicated by the data in the last column of Table 7.2. When Ba is replaced by the smaller Ca (0.99 Å) and Sr (1.12 Å) ions, by contrast, there is a corresponding decrease in the lattice constant, as indicated by the data in columns 3 and 4, respectively, of Table 7.2. All three alkaline earths, Ca, Sr, and Ba, appear prominently in the structures of 3 high-temperature superconductors.

B. Tetragonal Form

At room temperature barium titanate is tetragonal and the deviation from cubic, $(c - a)/\frac{1}{2}(c + a)$, is about 1%. All of the atoms have the same *x*, *y* coordinates as in the cubic case, but are shifted along the *z*-axis relative to each other by ≈ 0.1 Å, producing the puckered arrangement shown in Fig. 7.3. The distortions from the ideal structure are exaggerated in this sketch. The puckering bends the Ti-O-Ti group so that the Ti-O distance increases while the Ti-Ti distance remains almost

Table 7.1 Ionic Radii for Selected Elements^a

Small Small-Medium	Cu^{2+}	0.72 Å	Bi^{5+}	0.74 Å
	Cu^{+}	0.96 Å	Y^{3+}	0.94 Å
	Bi^{3+}	0.96 Å	Ti^{3+}	0.95 Å
	Ca^{2+}	0.99 Å	Bi^{3+}	0.96 Å
Medium-Large	Nd^{3+}	0.995 Å		
	Hg^{2+}	1.10 Å		
	Sr^{2+}	1.12 Å	La^{3+}	1.14 Å
	Pb^{2+}	1.20 Å	Ag^{+}	1.26 Å
Large	K^{+}	1.33 Å	O^{2-}	1.32 Å
	Ba^{2+}	1.34 Å	F^{-}	1.33 Å

^a See Table VI-2 of Poole *et al.* (1988) for a more extensive list.

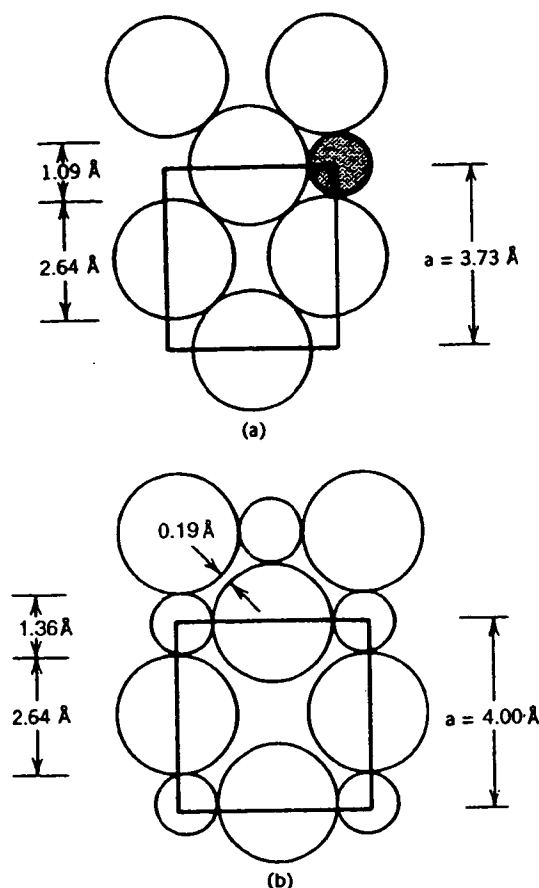


Figure 7.2 Cross section of the perovskite unit cell in the $z = 0$ plane showing (a) the size of the octahedral hole (shaded) between oxygens (large circles), and (b) oxygens pushed apart by the transition ions (small circles) in the hole sites. For each case the lattice constant is indicated on the right and the oxygen and hole sizes on the left (Poole *et al.*, 1988, p. 77).

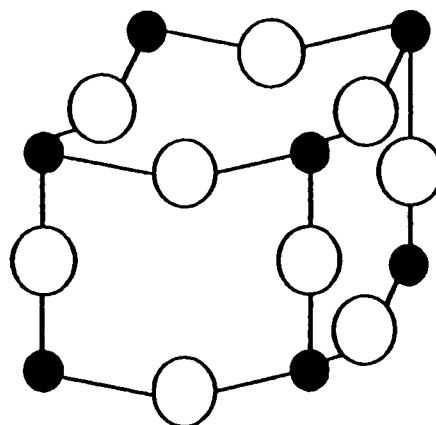


Figure 7.3 Perovskite tetragonal unit cell showing puckering of Ti-O layers that are perfectly flat in the cubic cell of Fig. 7.1. The notation of Fig. 7.1 is used (Poole *et al.*, 1988, p. 75).

the same. This has the effect of providing more room for the titanium atoms to fit in their lattice sites. We will see later that a similar puckering distortion occurs in the high-temperature superconductors as a way of providing space for the Cu atoms in the planes.

C. Orthorhombic Form

There are two principal ways in which a tetragonal structure distorts to form an orthorhombic phase. The first, shown at

Table 7.2 Dependence of Lattice Constants a of Selected Perovskites AMO_3 on Alkaline Earth A and Ionic Radius of Transition Metal Ion M^{+4} ; the Alkaline Earth Ionic Radii are 0.99 Å (Ca), 1.12 Å (Sr), and 1.34 Å (Ba)^a

Transitional metal	Transitional metal radius, Å	Lattice constant a , Å		
		Ca	Sr	Ba
Ti	0.68	3.84	3.91	4.01
Fe	—	—	3.87	4.01
Mo	0.70	—	3.98	4.04
Sn	0.71	3.92	4.03	4.12
Zr	0.79	4.02	4.10	4.19
Pb	0.84	—	—	4.27
Ce	0.94	3.85	4.27	4.40
Th	1.02	4.37	4.42	4.80

^a Data from Wyckoff (1964, pp. 391ff).

the top of Fig. 7.4, is for the b -axis to stretch relative to the a -axis, resulting in the formation of a rectangle. The second, shown at the bottom of the figure, is for one diagonal of the ab square to stretch and the other diagonal to compress, resulting in the formation of a rhombus. The two diagonals are perpendicular, rotated by 45° relative to the original axes, and become the a' , b' dimensions of the new orthorhombic unit cell, as shown in Fig. 7.5. These a' , b' lattice constants are $\approx \sqrt{2}$ times longer than the original constants, so that the volume of the unit cell roughly doubles; thus, it contains exactly twice as many atoms. (The same $\sqrt{2}$ factor appears in Eq. 7.1 in our discussion of the lattice constants for the orthorhombic form of barium titanate.)

When barium titanate is cooled below 5°C it undergoes a diagonal- or rhombal-type distortion. The atoms have the same z coordinates ($z = 0$ or $\frac{1}{2}$) as in the cubic phase, so the distortion occurs entirely in the x, y -plane, with no puckering of the atoms. The deviation from tetragonality, as

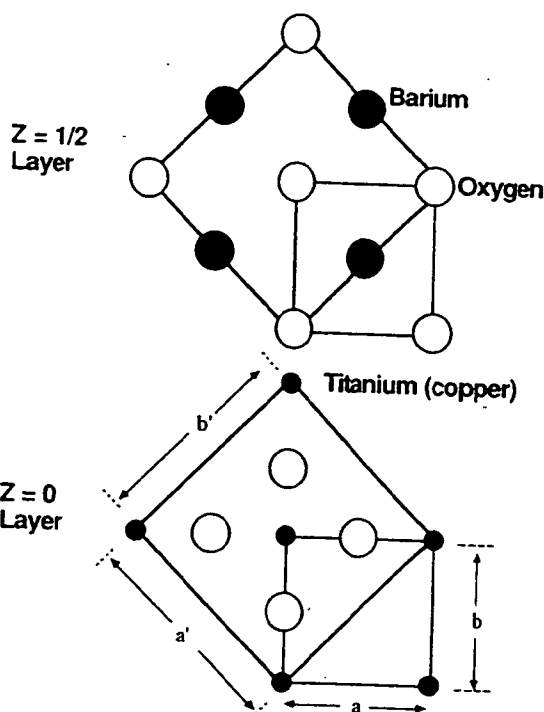


Figure 7.5 Rhombal expansion of monomolecular tetragonal unit cell (small squares, lower right) to bimolecular orthorhombic unit cell (large squares) with new axes 45° relative to the old axes. The atom positions are shown for the $z = 0$ and $z = \frac{1}{2}$ layers (Poole *et al.*, 1988, p. 76).

given by the percentage of anisotropy,

$$\% \text{ ANIS} = \frac{100|b - a|}{\frac{1}{2}(b + a)} = 0.22\%, \quad (7.3)$$

is less than that of most orthorhombic copper oxide superconductors. We see from Fig. 7.5 that in the cubic phase the oxygen atoms in the $z = 0$ plane are separated by 0.19 \AA . The rhombal distortion increases this O-O separation in one direction and decreases it in the other, in the manner indicated in Fig. 7.6a, to produce the Ti nearest-neighbor configuration shown in Fig. 7.6b. This arrangement helps to fit the titanium into its lattice site.

The transformation from tetragonal to orthorhombic is generally of the rhombal type for $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$ and of the rectangular type for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

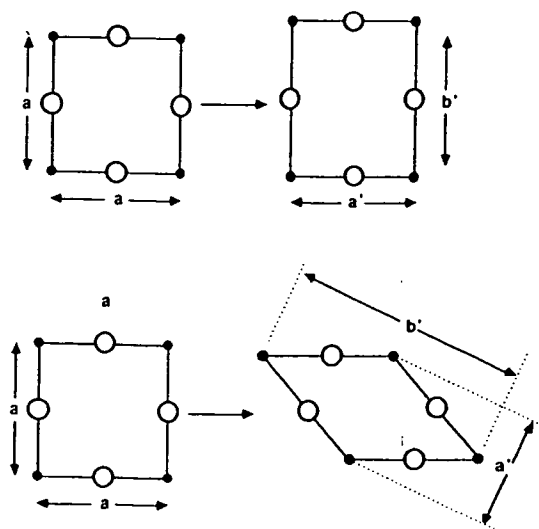


Figure 7.4 Rectangular- (top) and rhombal- (bottom) type distortions of a two-dimensional square unit cell of width a (Poole *et al.*, 1989).

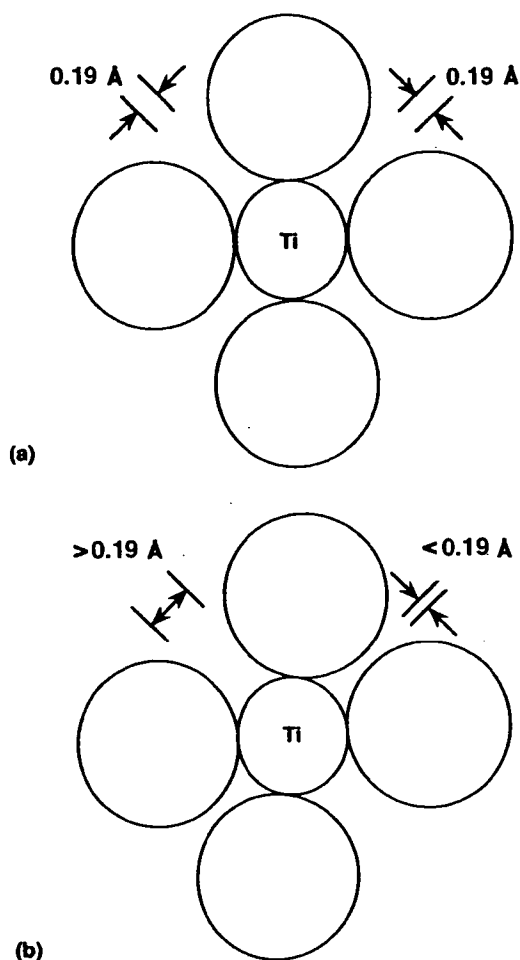


Figure 7.6 Shift of the oxygens in the a, b -plane around the titanium atom of perovskite from the room-temperature tetragonal (and cubic) configuration (a) to the rhombal configuration (b) of its low-temperature orthorhombic structure.

D. Planar Representation

Another way of picturing the structure of perovskite is to think of the atoms as forming horizontal planes. If we adopt the notation [E F C] to designate the occupation of the E, F, and C sites, the sketches of perovskite presented in Figs. 7.1 and 7.3 follow the scheme

$$\begin{array}{lll}
 z = 1 & [\text{TiO}_2-] & \text{Ti at E, O at two F sites} \\
 z = \frac{1}{2} & [\text{O}-\text{Ba}] & \text{O at E, Ba at C} \\
 z = 0 & [\text{TiO}_2-] & \text{Ti at E, O at two F sites.}
 \end{array} \quad (7.4)$$

The planes at the heights $z = 0, \frac{1}{2},$ and 1 can be labeled using this notation. The

usefulness of this labeling scheme will be clarified in Section V.

This completes our treatment of the structure of perovskite. We encountered many features that we will meet again in the analogous superconductor cases, and established notation that will be useful in describing the structure of the cuprates. However, before proceeding we present details about a cubic and a close-to-cubic perovskite superconductor in the following two sections.

III. CUBIC BARIUM POTASSIUM BISMUTH OXIDE

The compound



which forms for $x > 0.25$, crystallizes in the cubic perovskite structure with $a = 4.29 \text{ \AA}$ (Cava *et al.*, 1988; Jin *et al.*, 1992; Mattheiss *et al.*, 1988). K^+ ions replace some of the Ba^{2+} ions in the C site, and Bi ions occupy the E sites of Eq. (7.2) (Hinks *et al.*, 1988b; Kwei *et al.*, 1989; Pei *et al.*, 1990; Salem-Sugui *et al.*, 1991; Schneemeyer *et al.*, 1988). Some oxygen sites are vacant, as indicated by y . Hinks *et al.* (1989) and Pei *et al.* (1990) determined the structural phase diagram (cf. Kuentzler *et al.*, 1991; Zubkus *et al.*, 1991). We should note from Table 7.1 that the potassium (1.33 \AA) and barium (1.32 \AA) ions are almost the same size, and that Bi^{5+} (0.74 \AA) is close to Ti^{4+} (0.68 \AA). Bismuth represents a mixture of the valence states Bi^{3+} and Bi^{5+} which share the Ti^{4+} site in a proportion that depends on x and y . The larger size (0.96 \AA) of the Bi^{3+} ion causes the lattice constant a to expand 7% beyond its cubic BaTiO_3 value. Oxygen vacancies help to compensate for the larger size of Bi^{3+} .

It is noteworthy that $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-y}$ becomes superconducting at a temperature ($\approx 40 \text{ K}$ for $x \approx 0.4$) that is higher than the T_c of all of the A15 compounds. This compound, which has no copper, has

been widely studied in the quest for clues that would elucidate the mechanism of high-temperature superconductivity. Features of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-y}$, such as the fact that it contains a variable valence state ion and utilizes oxygen vacancies to achieve charge compensation, reappear in the high-temperature superconducting compounds.

IV. BARIUM LEAD BISMUTH OXIDE

In 1983 Mattheiss and Hamann referred to the 1975 "discovery by Sleight *et al.* of high-temperature superconductivity" in the compound $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ in the composition range $0.05 \leq x \leq 0.3$ with T_c up to 13 K. Many consider this system, which disproportionates $2\text{Bi}^{4+} \rightarrow \text{Bi}^{3+} + \text{Bi}^{5+}$ in going from the metallic to the semiconducting state, as a predecessor to the LaSrCuO system.

The metallic compound BaPbO_3 is a cubic perovskite with the relatively large lattice constant (Wyckoff, 1964; cf. Nitta *et al.*, 1965; Shannon and Bierstedt, 1970) listed in Table 7.3. At room temperature semiconducting BaBiO_3 is monoclinic ($a \approx b \approx c/\sqrt{2}$, $\beta = 90.17^\circ$), but close to orthorhombic (Chaillout *et al.*, 1985; Cox and Sleight, 1976, 1979; cf. Federici *et al.*, 1990; Jeon *et al.*, 1990; Shen *et al.*, 1989). These two compounds form a solid solution series $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ involving cubic, tetragonal, orthorhombic, and monoclinic modifications. Superconductivity appears in the tetragonal phase, and the metal-to-insulator transition occurs at the tetragonal-to-orthorhombic phase boundary $x \approx 0.35$ (Gilbert *et al.*, 1978; Koyama and Ishimaru, 1992; Mattheiss, 1990; Mattheiss and Hamann, 1983; Sleight, 1987; cf. Bansil *et al.*, 1991; Ekino and Akimitsu, 1989a, b; Papaconstantopoulos *et al.*, 1989).

The compound resembles



with its variable Bi valence states, but it differs in not exhibiting superconductivity in the cubic phase.

V. PEROVSKITE-TYPE SUPERCONDUCTING STRUCTURES

In their first report on high-temperature superconductors Bednorz and Müller (1986) referred to their samples as "metallic, oxygen-deficient ... perovskite-like mixed-valence copper compounds." Subsequent work has confirmed that the new superconductors do indeed possess these characteristics.

In the oxide superconductors Cu^{2+} replaces the Ti^{4+} of perovskite, and in most cases the TiO_2 -perovskite layering is retained as a CuO_2 layering with two oxygens per copper. Because of this feature of CuO_2 layers, which is common to all of the high-temperature superconductors, such superconductors exhibit a uniform lattice size in the a, b -plane, as the data in Table 7.3 demonstrate. The compound BaCuO_3 does not occur because the Cu^{4+} ion does not form, but this valence constraint is overcome by replacement of Ba^{2+} by a trivalent ion, such as La^{3+} or Y^{3+} , by a reduction in the oxygen content, or by both. The result is a set of "layers" containing only one oxygen per cation located between each pair of CuO_2 layers, or none at all. Each high-temperature superconductor has a unique sequence of layers.

We saw from Eq. (7.2) that each atom in perovskite is located in one of three types of sites. In like manner, each atom at the height z in a high-temperature superconductor occupies either an Edge (E) site on the edge $(0, 0, z)$, a Face (F) site on the midline of a face $((0, \frac{1}{2}, z)$ or $(\frac{1}{2}, 0, z)$ or both), or a Centered (C) site centered within the unit cell on the z -axis $(\frac{1}{2}, \frac{1}{2}, z)$. The site occupancy notation [E F C] is used because many cuprates contain a succession of $[\text{Cu O}_2 -]$ and $[- \text{O}_2 \text{Cu}]$ layers in which the Cu atom switches between edge and centered sites, with the oxygens

Table 7.3 Crystallographic Characteristics of Oxide Superconducting and Related Compounds^a

Compound	Symbol	Symm	Type	Enlarg.	Form. units	a_0 (Å)	c_0 (Å)	c_0/Cu	%Anis	T_c (K)	Comments
BaTiO ₃	—	C	A	1	1	4.012	4.012	—	0	—	$T > 200^\circ\text{C}$
BaTiO ₃	—	T	A	1	1	3.995	4.03	—	0	—	20°C
BaTiO ₃	—	O	A	$\sqrt{2}$	2	$4.013\sqrt{2}$	3.990	—	0.23	—	$T < 5^\circ\text{C}$
BaPbO ₃	—	C	A	1	1	4.273	4.273	—	0	0.4	
BaPb _{0.7} Bi _{0.3} O ₃	—	T	S	$\sqrt{2}$	4	$4.286\sqrt{2}$	4.304	—	0	12	
BaBiO ₃	—	M	A	$\sqrt{2}$	2	$4.355\sqrt{2}$	4.335	—	0.13	—	$\beta = 90.17^\circ$
Ba _{0.6} K _{0.4} BiO ₃	—	C	A	1	1	4.293	4.293	—	0	30	
La ₂ CuO ₄	0201	T	S	1	2	3.81	13.18	6.59	0	35	Sr, doped
La ₂ CuO ₄	0201	O	S	$\sqrt{2}$	4	$3.960\sqrt{2}$	13.18	6.59	6.85	35	Sr, doped
YBa ₂ Cu ₃ O ₈	0213	T	A	1	1	3.902	11.94	3.98	0	—	
YBa ₂ Cu ₃ O ₇	0213	O	A	1	1	3.855	11.68	3.89	1.43	92	
Bi ₂ Sr ₂ CaCu ₂ O ₈	2212	T	S	$5\sqrt{2}$	20	$3.81\sqrt{2}$	30.6	7.65	0	84	
Bi ₂ Sr ₂ Ca ₂ Cu ₃ O ₁₀	2223	O	S	$5\sqrt{2}$	20	$3.83\sqrt{2}$	37	6.17	0.57	110	
Tl ₂ Ba ₂ CuO ₆	2201	T	S	1	2	3.83	23.24	11.6	0	90	
Tl ₂ Ba ₂ CaCu ₂ O ₈	2212	T	S	1	2	3.85	29.4	7.35	0	110	
Tl ₂ Ba ₂ Ca ₂ Cu ₃ O ₁₀	2223	T	S	1	2	3.85	35.88	5.98		125	
TlBa ₂ CuO ₅	1201		A	1	1		9.5	9.5		<17	
TlBa ₂ CaCu ₂ O ₇	1212		A	1	1		12.7	6.35		91	
TlBa ₂ Ca ₂ Cu ₃ O ₉	1223		A	1	1		15.9	5.3		116	
TlBa ₂ Ca ₃ Cu ₄ O ₁₁	1234		A	1	1		19.1	4.78		122	
TlBa ₂ Ca ₄ Cu ₅ O ₁₃	1245		A	1	1		22.3	4.46		<120	
HgBa ₂ CuO ₄	1201	T	A	1	1	3.86	9.5	9.5		95	
HgBa ₂ CaCu ₂ O ₆	1212	T	A	1	1	3.86	12.6	6.3		122	
HgBa ₂ Ca ₂ Cu ₃ O ₈	1223	T	A	1	1	3.86	17.7	5.2		133	

^a Symbol, symmetry (cubic C, tetragonal T, orthorhombic O, monoclinic M); type (aligned A, staggered S); enlargement in a , b -plane (diagonal distortion $\sqrt{2}$, superlattice 5); formula units per unit cell; lattice parameters (a_0 , c_0 , and c_0 per Cu ion); % anisotropy; and transition temperature T_c . For the orthorhombic compounds tabulated values of a_0 are averages of a_0 and b_0 .

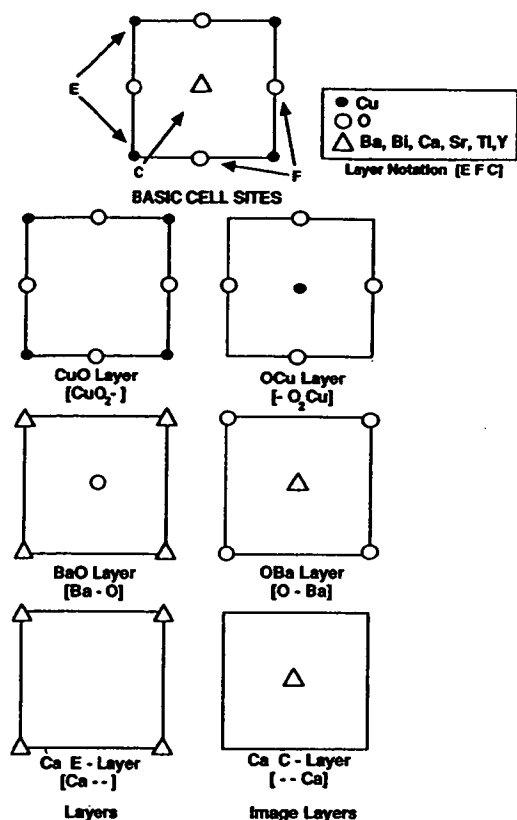


Figure 7.7 Types of atom positions in the layers of a high-temperature superconductor structure, using the edge, face, center notation [E F C]. Typical site occupancies are given in the upper right (Poole *et al.*, 1989).

remaining at their face positions. Similar alternations in position take place with Ba, O, and Ca layers, as illustrated in Fig. 7.7.

Hauck *et al.* (1991) proposed a classification of superconducting oxide structures in terms of the sequence (1) superconducting layers [Cu O₂-] and [-O₂ Cu], (2) insulating layers, such as [Y - -] or [- - Ca], and (3) hole-donating layers, such as [Cu O^b -] or [Bi - O].

The high-temperature superconductor compounds have a horizontal reflection plane (\perp to z) called σ_h at the center of the unit cell and another σ_h reflection plane at the top (and bottom). This means that every plane of atoms in the lower half of the cell at the height z is duplicated in the upper half at the height $1-z$. Such atoms, of course, appear twice in the unit cell, while atoms right on the symmetry planes only occur once since they cannot be reflected. Figure 7.8 shows a [Cu O₂ -] plane at a height z reflected to the height $1-z$. Note how the puckering preserves the reflection symmetry operation. Superconductors that have this reflection plane, but lack end-centering and body-centering op-

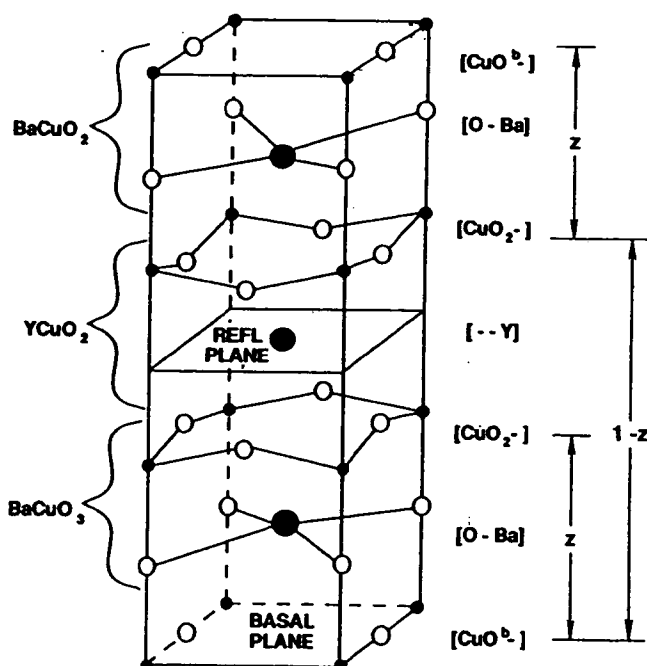


Figure 7.8 Unit cell of YBa₂Cu₃O₇ showing the molecular groupings, reflection plane, and layer types.

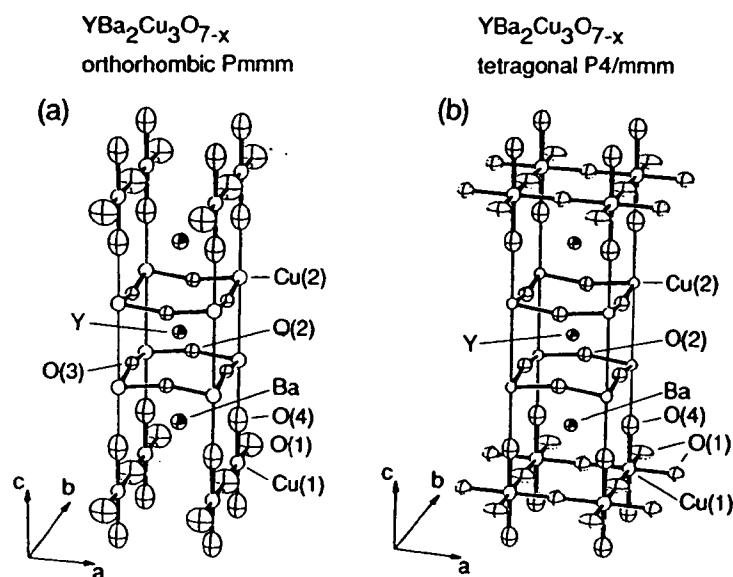


Figure 7.10 Sketches of the superconducting orthorhombic (left) and nonsuperconducting tetragonal (right) YBaCuO unit cells. Thermal vibration ellipsoids are shown for the atoms. In the tetragonal form the oxygen atoms are randomly dispersed over the basal plane sites (Jorgensen *et al.*, 1987a,b; also see Schuller *et al.*, 1987).

Table 7.4 Normalized Atom Positions in the $\text{YBa}_2\text{Cu}_3\text{O}_7$ Orthorhombic Unit Cell (dimensions $a=3.83 \text{ \AA}$, $b=3.88 \text{ \AA}$, and $c=11.68 \text{ \AA}$)

Layer	Atom	x	y	z
[Cu O -]	Cu(1)	0	0	1
	O(1)	0	$\frac{1}{2}$	1
[O - Ba]	O(4)	0	0	0.8432
	Ba	$\frac{1}{2}$	$\frac{1}{2}$	0.8146
[Cu O ₂ -]	Cu(2)	0	0	0.6445
	O(3)	0	$\frac{1}{2}$	0.6219
	O(2)	$\frac{1}{2}$	0	0.6210
[- - Y]	Y	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
[Cu O ₂ -]	O(2)	$\frac{1}{2}$	0	0.3790
	O(3)	0	$\frac{1}{2}$	0.3781
	Cu(2)	0	0	0.3555
[O - Ba]	Ba	$\frac{1}{2}$	$\frac{1}{2}$	0.1854
	O(4)	0	0	0.1568
	O(1)	0	$\frac{1}{2}$	0
[Cu O -]	Cu(1)	0	0	0

"the chains," consists of $-\text{Cu}-\text{O}-\text{Cu}-\text{O}-$ chains along the b axis in lines that are perfectly straight because they are in a horizontal reflection plane σ_h ; where no puckering can occur. Note that, according to the figures, the copper atoms are all stacked one above the other on edge (E) sites, as expected for an aligned-type superconductor. Both the copper oxide planes and the chains contribute to the superconducting properties.

B. Copper Coordination

Now that we have described the planar structure of YBaCuO it will be instructive to examine the local environment of each copper ion. The chain copper ion $\text{Cu}(1)$ is square planar-coordinated and the two coppers $\text{Cu}(2)$ and $\text{Cu}(3)$ in the plane exhibit fivefold pyramidal coordination, as indicated in Fig. 7.11. The ellipsoids at the atom positions of Fig. 7.10 provide a measure of the thermal vibrational motion which the atoms experience, since the amplitudes of the atomic vibrations are indicated by the relative size of each of the ellipsoids.

C. Stacking Rules

The atoms arrange themselves in the various planes in such a way as to enable them to stack one above the other in an efficient manner, with very little interference from neighboring atoms. Steric effects prevent large atoms such as Ba (1.34 Å) and O (1.32 Å) from overcrowding a layer or from aligning directly on top of each other in adjacent layers. In many cuprates stacking occurs in accordance with the following two empirical rules:

1. Metal ions occupy either edge or centered sites, and in adjacent layers alternate between E and C sites.
2. Oxygens are found in any type of site, but they occupy only one type in a particular layer, and in adjacent layers they are on different types of sites.

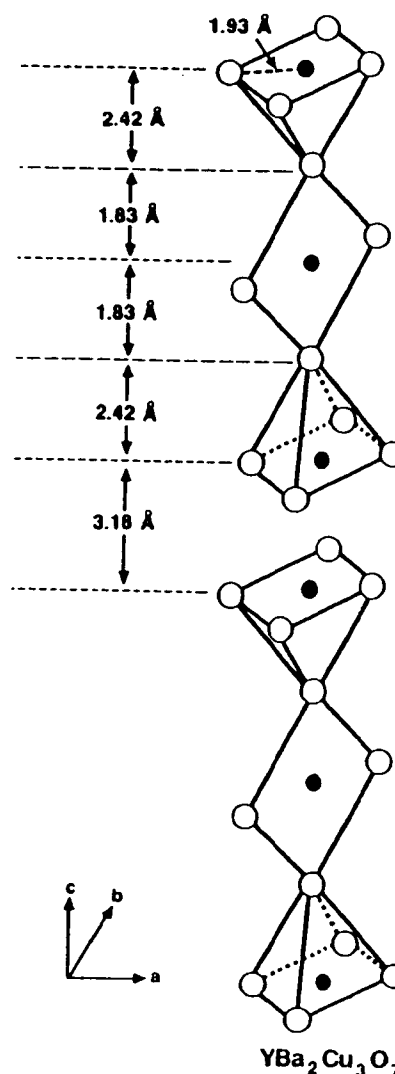


Figure 7.11 Stacking of pyramid, square-planar, and inverted pyramid groups along the c -axis of orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_7$ (adapted from Poole *et al.*, 1988, p. 100).

Minor adjustments to make more room can be brought about by puckering or by distorting from tetragonal to orthorhombic.

D. Crystallographic Phases

The $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound comes in tetragonal and orthorhombic varieties, as shown in Fig. 7.10, and it is the latter phase which is ordinarily superconducting. In the tetragonal phase the oxygen sites in the chain layer are about half occupied

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Fractional Site Occupancy

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in a random or disordered manner, and in the orthorhombic phase are ordered into $-\text{Cu}-\text{O}-$ chains along the b direction. The oxygen vacancy along the a direction causes the unit cell to compress slightly so that $a < b$, and the resulting distortion is of the rectangular type shown in Fig. 7.4a. Increasing the oxygen content so that $\delta < 0$ causes oxygens to begin occupying the vacant sites along a . Superlattice ordering of the chains is responsible for the phase that goes superconducting at 60 K.

YBaCuO is prepared by heating in the 750–900°C range in the presence of various concentrations of oxygen. The compound is tetragonal at the highest temperatures, increases its oxygen content through oxygen uptake and diffusion (Rothman *et al.*, 1991) as the temperature is lowered, and undergoes a second-order phase transition of the order–disorder type at about 700°C to the low-temperature orthorhombic phase, as indicated in Fig. 7.12

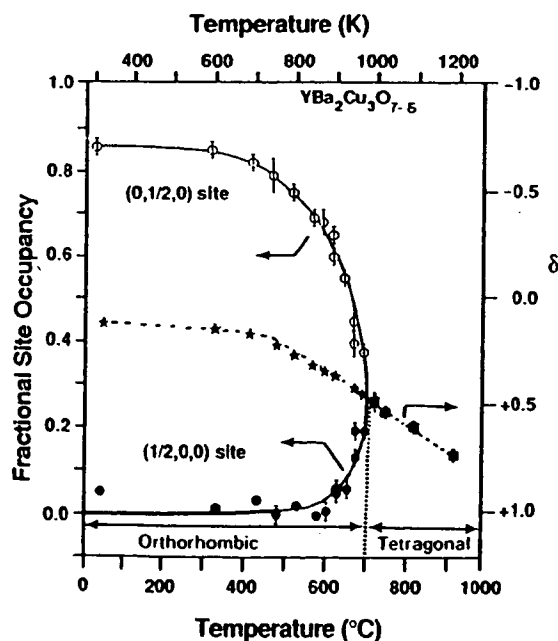


Figure 7.12 Fractional occupancies of the $(\frac{1}{2}, 0, 0)$ (bottom) and $(0, \frac{1}{2}, 0)$ (top) sites (scale on left), and the oxygen content parameter δ (center, scale on right) for quench temperatures of YBaCuO in the range 0–1000°C. The δ parameter curve is the average of the two site-occupancy curves (adapted from Jorgensen *et al.*, 1987a; also see Schuller *et al.*, 1987; see also Poole *et al.*, 1988).

(Jorgensen *et al.*, 1987, 1990; Schuller *et al.*, 1987; cf. Beyers and Ahn, 1991; Metzger *et al.*, 1993; Fig. 8). Quenching by rapid cooling from a high temperature can produce at room temperature the tetragonal phase sketched on the right side of Fig. 7.10, and slow annealing favors the orthorhombic phase on the left. Figure 7.12 shows the fractional site occupancy of the oxygens in the chain site $(0, \frac{1}{2}, 0)$ as a function of the temperature in an oxygen atmosphere. A sample stored under sealed conditions exhibited no degradation in structure or change in T_c four years later (Sequeira *et al.*, 1992). Ultra-thin films tend to be tetragonal (Streiffer *et al.*, 1991).

E. Charge Distribution

Information on the charge distributions around atoms in conductors can be obtained from knowledge of their energy bands (see description in Chapter 8). This is most easily accomplished by carrying out a Fourier-type mathematical transformation between the reciprocal k_x, k_y, k_z -space (cf. Chapter 8, Section II) in which the energy bands are plotted and the coordinate x, y, z -space, where the charge is distributed. We will present the results obtained for $\text{YBa}_2\text{Cu}_3\text{O}_7$ in the three vertical symmetry planes (x, z , y, z , and diagonal), all containing the z -axis through the origin, shown shaded in the unit cell of Fig. 7.13.

Contour plots of the charge density of the valence electrons in these planes are sketched in Fig. 7.14. The high density at the Y^{3+} and Ba^{2+} sites and the lack of contours around these sites together indicate that these atoms are almost completely ionized, with charges of +3 and +2, respectively. It also shows that these ions are decoupled from the planes above and below. This accounts for the magnetic isolation of the Y site whereby magnetic ions substituted for yttrium do not interfere with the superconducting properties. In contrast, the contours surrounding the Cu and O ions are not characteristic of an

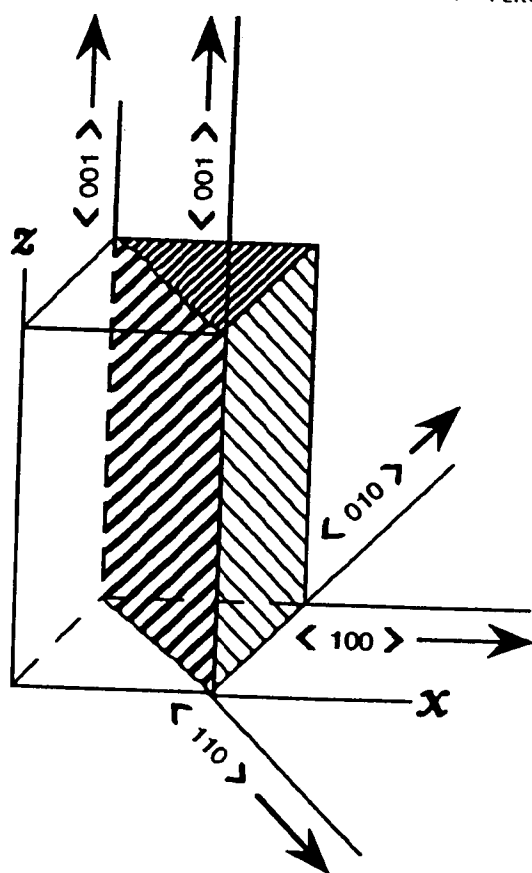


Figure 7.13 Three vertical crystallographic planes (x, z , y, z , and diagonal) of a tetragonal unit cell of $\text{YBa}_2\text{Cu}_3\text{O}_7$, and standard notation for the four crystallographic directions.

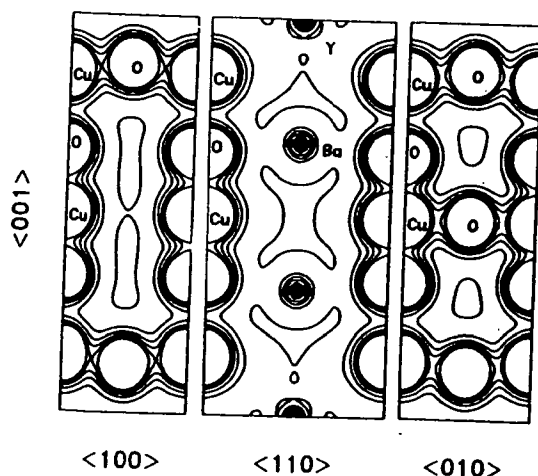
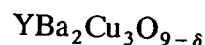


Figure 7.14 Charge density in the three symmetry planes of YBaCuO shown shaded in Fig. 7.13. The x, z , diagonal and the y, z planes are shown from left to right, labeled $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 010 \rangle$, respectively. These results are obtained from band structure calculations, as will be explained in the following chapter (Krakauer and Pickett, 1988).

ordinary ionic compound. The short Cu–O bonds in the planes and chains (1.93–1.96 Å) increase the charge overlap. The least overlap appears in the Cu(2)–O(4) vertical bridging bond, which is also fairly long (2.29 Å). The Cu, O charge contours can be represented by a model that assigns charges of +1.62 and –1.69 to Cu and O, respectively, rather than the values of +2.33 and –2.00 expected for a standard ionic model, where the charge +2.33 is an average of +2, +2, and +3 for the three copper ions. Thus the Cu–O bonds are not completely ionic, but partly covalent.

F. YBaCuO Formula

In early work the formula



was used for YBaCuO because the prototype triple perovskite $(\text{YCuO}_3)(\text{BaCuO}_3)_2$ has nine oxygens. Then crystallographers showed that there are eight oxygen sites in the 14-atom YBaCuO unit cell, and the formula $\text{YBa}_2\text{Cu}_3\text{O}_{8-\delta}$ came into widespread use. Finally, structure refinements demonstrated that one of the oxygen sites is systematically vacant in the chain layers, so the more appropriate expression $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ was introduced. It would be preferable to make one more change and use the formula $\text{Ba}_2\text{YCu}_3\text{O}_{7-\delta}$ to emphasize that Y is analogous to Ca in the bismuth and thallium compounds, but very few workers in the field do this, so we reluctantly adopt the usual “final” notation. In the Bi–Tl compound of Section IX, B, $\text{Ba}_2\text{YCu}_3\text{O}_{7-\delta}$ would be called a 0213 compound. We will follow the usual practice of referring to $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ as the 123 compound.

G. $\text{YBa}_2\text{Cu}_4\text{O}_8$ and $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$

These two superconductors are sometimes referred to as the 124 compound and the 247 compound, respectively. They have the property that for each atom at position (x, y, z) there is another identical atom at

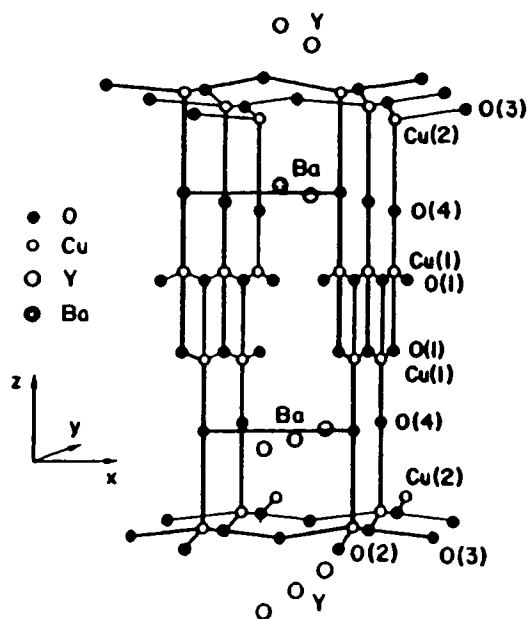
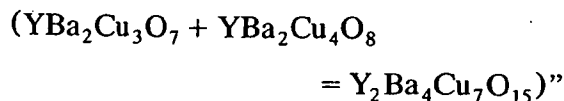


Figure 7.15 Crystal structure of $\text{YBa}_2\text{Cu}_4\text{O}_8$ showing how, as a result of the side-centering symmetry operation, the atoms in adjacent Cu–O chains are staggered along the y direction, with Cu above O and O above Cu (Heyen *et al.*, 1991; modified from Campuzano *et al.*, 1990).

position $(x, y + \frac{1}{2}, z + \frac{1}{2})$. In other words, the structure is side centered. This property prevents the stacking rules of Section C from applying.

The chain layer of $\text{YBa}_2\text{Cu}_3\text{O}_7$ becomes two adjacent chain layers in $\text{YBa}_2\text{Cu}_4\text{O}_8$, with the Cu atoms of one chain located directly above or below the O atoms of the other, as shown in Fig. 7.15 (Campuzano *et al.*, 1990; Heyen *et al.*, 1990a, 1991; Iqbal, 1992; Kaldis *et al.*, 1989; Marsh *et al.*, 1988; Morris *et al.*, 1989a). The transition temperature remains in the range from 40 K to 80 K when Y is replaced by various rare earths (Morris *et al.*, 1989). The double chains do not exhibit the variable oxygen stoichiometry of the single ones.

The other side-centered compound, $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$, may be considered according to Torardi, “as an ordered 1:1 intergrowth of the 123 and 124 compounds



(Bordel *et al.*, 1988, Gupta and Gupta, 1993). The 123 single chains can vary in their oxygen content, and superconductivity onsets up to 90 K have been observed. This compound has been synthesized with several rare earths substituted for Y (Morris *et al.*, 1989b).

VII. BODY CENTERING

In Section V we discussed aligned-type superconductor structures that possess a horizontal plane of symmetry. Most high-temperature superconductor structures have, besides this σ_h plane, an additional symmetry operation called body centering whereby for every atom with coordinates (x, y, z) there is an identical atom with coordinates as determined from the following operation:

$$x \rightarrow x \pm \frac{1}{2}, \quad y \rightarrow y \pm \frac{1}{2}, \quad z \rightarrow z \pm \frac{1}{2} \quad (7.5)$$

Starting with a plane at the height z this operation forms what is called an image plane at the height $z + \frac{1}{2}$ in which the edge atoms become centered, the centered atoms become edge types, and each face atom moves to another face site. In other words, the body-centering operation acting on a plane at the height z forms a body centered plane, also called an image plane, at the height $z \pm \frac{1}{2}$. The signs in these operations are selected so that the generated points and planes remain within the unit cell. Thus if the initial value of z is greater than $\frac{1}{2}$, the minus sign must be selected, viz., $z \rightarrow z - \frac{1}{2}$. Body centering causes half of the Cu–O planes to be $[\text{Cu O}_2 -]$, with the copper atoms at edge sites, and the other half to be $[- \text{O}_2 \text{ Cu}]$, with the copper atoms at centered sites.

Let us illustrate the symmetry features of a body-centered superconductor by considering the example of $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$. This compound has an initial plane $[\text{Cu O}_2 -]$ with the copper and oxygen atoms at the vertical positions $z = 0.0540$ and 0.0531 , respectively, as shown in Fig.

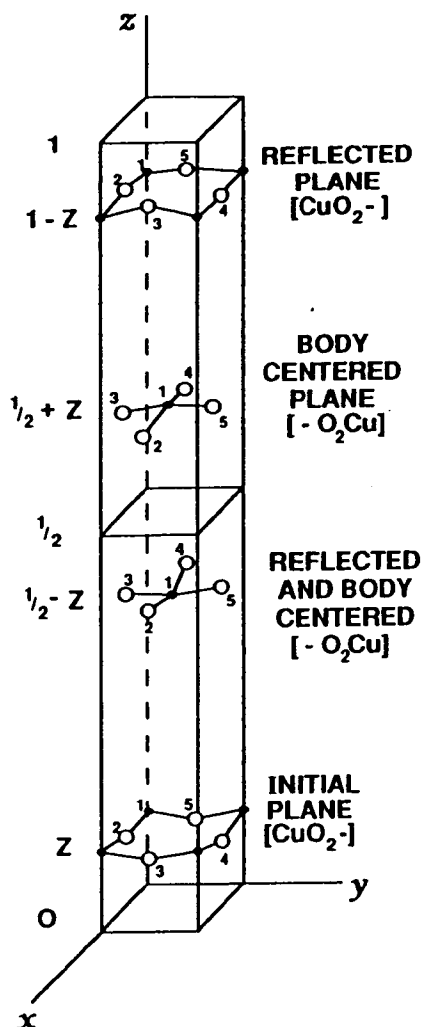


Figure 7.16 Body-centered tetragonal unit cell containing four puckered CuO_2 groups showing how the initial group (bottom) is replicated by reflection in the horizontal reflection plane ($z = \frac{1}{2}$), by the body centering operation, and by both.

7.16. For illustrative purposes the figure is drawn for values of z closer to 0.1. We see from the figure that there is a reflected plane $[\text{Cu O}_2 -]$ at the height $1 - z$, an image (i.e., body centered) plane $[- \text{O}_2 \text{ Cu}]$ of the original plane at the height $\frac{1}{2} + z$, and an image plane $[- \text{O}_2 \text{ Cu}]$ of the reflected plane (i.e., a reflected and body centered plane) at the height $\frac{1}{2} - z$. Figure 7.16 illustrates this situation and indicates how the atoms of the initial plane can be transformed into particular atoms in other planes (see Problem 5). Figure 7.17 shows how the configurations of the

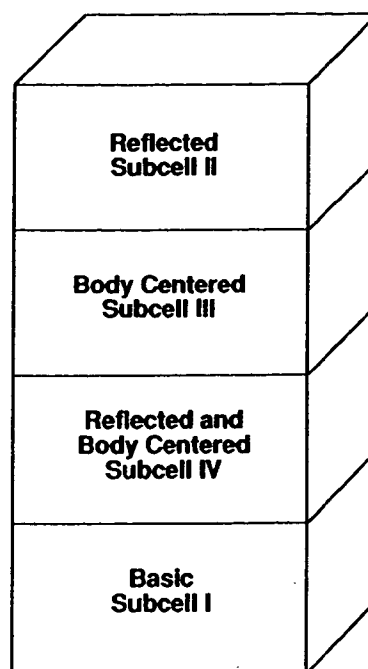


Figure 7.17 Body-centered unit cell divided into four regions by the reflection and body centering operations.

atoms in one-quarter of the unit cell, called the *basic subcell*, or subcell I, determine their configurations in the other three subcells II, III, and IV through the symmetry operations of reflection and body centering.

VIII. BODY-CENTERED La_2CuO_4 AND Nd_2CuO_4

The body-centered compound
 $M_2\text{CuO}_4$

has three structural variations in the same crystallographic space group, namely the $M = \text{La}$ and $M = \text{Nd}$ types, and a third mixed variety (Xiao *et al.*, 1989). Table 7.5 lists the atom positions of the first two types, and Fig. 7.18 presents sketches of the structures of all three. Each will be discussed in turn.

A. Unit Cell Generation of La_2CuO_4 (T Phase)

The structure of the more common La_2CuO_4 variety, often called the T phase,

Table 7.5 Atom Positions in the La_2CuO_4 and Nd_2CuO_4 Structures

La ₂ CuO ₄ structure					Nd ₂ CuO ₄ structure					
Layer	Atom	x	y	z	Layer	Atom	x	y	z	
[Cu O ₂ -]	O(1)	$\frac{1}{2}$	0	1	[Cu O ₂ -]	O(1)	$\frac{1}{2}$	0	1	
	Cu	0	0	1		Cu	0	0	1	
	O(1)	0	$\frac{1}{2}$	1		O(1)	0	$\frac{1}{2}$	1	
	La	$\frac{1}{2}$	$\frac{1}{2}$	0.862		[- - Nd]	Nd	$\frac{1}{2}$	$\frac{1}{2}$	0.862
[O - La]	O(2)	0	0	0.818	[- O ₂ -]	O(3)	0	$\frac{1}{2}$	$\frac{3}{4}$	
[La - O]	O(2)	$\frac{1}{2}$	$\frac{1}{2}$	0.682		O(3)	$\frac{1}{2}$	0	$\frac{3}{4}$	
	La	0	0	0.638		[Nd - -]	Nd	0	0	0.638
	O(1)	$\frac{1}{2}$	0	$\frac{1}{2}$		O(1)	$\frac{1}{2}$	0	$\frac{1}{2}$	
	[- O ₂ Cu]	Cu	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	[- O ₂ Cu]	Cu	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
O(1)		0	$\frac{1}{2}$	$\frac{1}{2}$	O(1)	0	$\frac{1}{2}$	$\frac{1}{2}$		
[La - O]		La	0	0	0.362	[Nd - -]	Nd	0	0	0.362
		O(2)	$\frac{1}{2}$	$\frac{1}{2}$	0.318	[- O ₂ -]	O(3)	$\frac{1}{2}$	0	$\frac{1}{4}$
	[O - La]	O(2)	0	0	0.182		O(3)	0	$\frac{1}{2}$	$\frac{1}{4}$
		La	$\frac{1}{2}$	$\frac{1}{2}$	0.138		[- - Nd]	Nd	$\frac{1}{2}$	$\frac{1}{2}$
O(1)		0	$\frac{1}{2}$	0	O(1)		0	$\frac{1}{2}$	0	
[Cu O ₂ -]		Cu	0	0	0	[Cu O ₂ -]	Cu	0	0	0
	O(1)	$\frac{1}{2}$	0	0	O(1)	$\frac{1}{2}$	0	0		

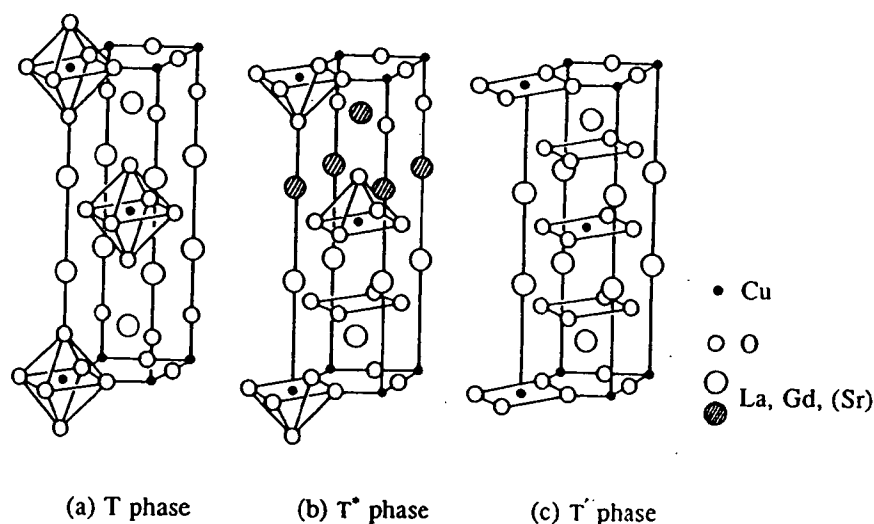


Figure 7.18 (a) Regular unit cell (T phase) associated with hole-type $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$ superconductors, (b) hybrid unit cell (T* phase) of the hole-type $\text{La}_{2-x-y}\text{R}_y\text{Sr}_x\text{CuO}_4$ superconductors, and (c) alternate unit cell (T' phase) associated with electron-type $(\text{Nd}_{1-x}\text{Ce}_x)_2\text{CuO}_4$ superconductors. The La atoms in the left structure become Nd atoms in the right structure. The upper part of the hybrid cell is T type, and the bottom is T'. The crystallographic space group is the same for all three unit cells (Xiao *et al.*, 1989; see also Oguchi, 1987; Ohbayashi *et al.*, 1987; Poole *et al.*, 1988, p. 83; Tan *et al.*, 1990).

can be pictured as a stacking of CuO_4La_2 groups alternately with image (i.e., body centered) $\text{La}_2\text{O}_4\text{Cu}$ groups along the c direction, as indicated on the left side of Fig. 7.19 (Cava *et al.*, 1987; Kinoshita *et al.*, 1992; Longo and Raccach, 1973; Ohbayashi *et al.*, 1987; Onoda *et al.*, 1987; Zolliker *et al.*, 1990). Another way of visualizing the structure is by generating it from the group $\text{Cu}_2\text{O}_2\text{La}$, comprising the layers $[\text{O}-\text{La}]$ and $\frac{1}{2}[\text{Cu O}_2 -]$ in subcell I shown on the right side of Fig. 7.19 and also on the left side of Fig. 7.20. (The factor $\frac{1}{2}$ appears because the $[\text{Cu O}_2 -]$ layer is shared by two subcells.) Subcell II is formed by reflection from subcell I, and subcells III and IV are formed from I and II via the body-centering operation in the manner of Figs. 7.16 and 7.17. Therefore, subcells I

and II together contain the group CuO_4La_2 , and subcells III and IV together contain its image (body centered) counterpart group $\text{La}_2\text{O}_4\text{Cu}$. The BiSrCaCuO and TlBaCaCuO structures to be discussed in Section IX can be generated in the same manner, but with much larger repeat units along the c direction.

B. Layering Scheme

The La_2CuO_4 layering scheme consists of equally-spaced, flat CuO_2 layers with their oxygens stacked one above the other, the copper ions alternating between the $(0,0,0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ sites in adjacent layers, as shown in Fig. 7.21. These planes are body-centered images of each other, and are perfectly flat because they are

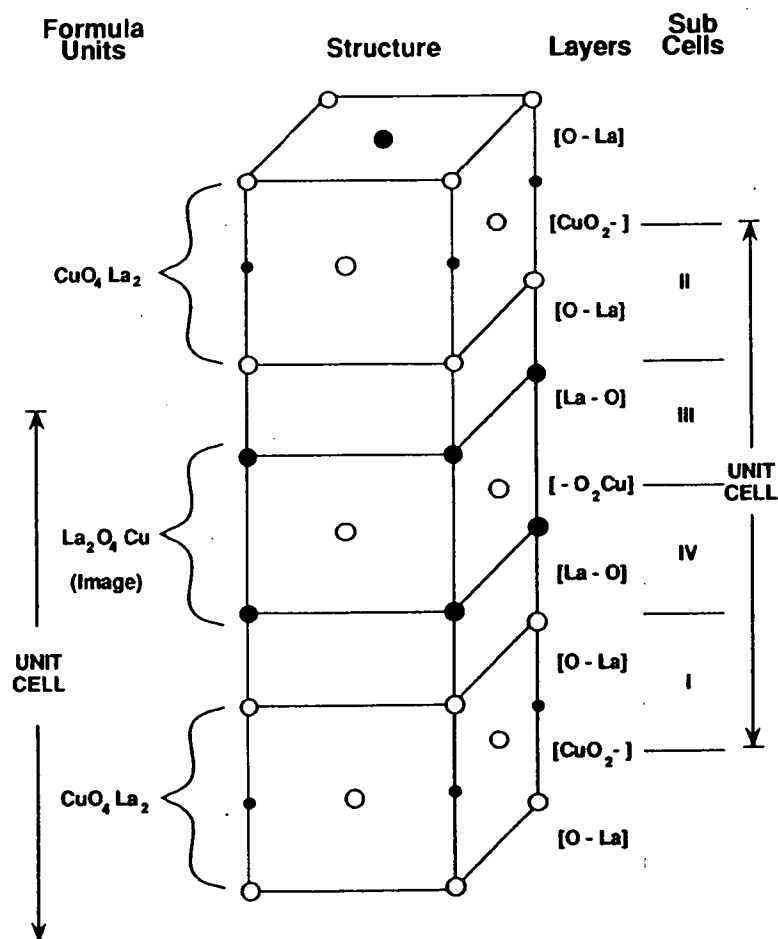


Figure 7.19 Structure of La_2CuO_4 (center), showing the formula units (left) and the level labels and subcell types (right). Two choices of unit cell are indicated, the left-side type unit cell based on formula units, and the more common right-side type unit cell based on copper-oxide layers.

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La_2CuO_4	Sub Cell	Nd_2CuO_4
$[\text{CuO}_2^-]$	—	$[\text{CuO}_2^-]$
$[\text{O} - \text{La}]$	II	$[- - \text{Nd}]$
$[\text{La} - \text{O}]$	—	$[- \text{O}_2^-]$
	III	$[\text{Nd} - -]$
$[- \text{O}_2\text{Cu}]$	—	$[- \text{O}_2\text{Cu}]$
$[\text{La} - \text{O}]$	IV	$[\text{Nd} - -]$
$[\text{O} - \text{La}]$	—	$[- \text{O}_2^-]$
	I	$[- - \text{Nd}]$
$[\text{CuO}_2^-]$	—	$[\text{CuO}_2^-]$

Figure 7.20 Layering schemes of the La_2CuO_4 (T, left) and Nd_2CuO_4 (T', right) structures. The locations of the four subcells of the unit cell are indicated in the center column.

reflection planes. Half of the oxygens, O(1), are in the planes, and the other half, O(2), between the planes. The copper is octahedrally coordinated with oxygen, but the distance 1.9 Å from Cu to O(1) in the CuO_2 planes is much less than the vertical distance of 2.4 Å from Cu to the apical oxygen O(2), as indicated in Fig. 7.22. The La is ninefold coordinated to four O(1) oxygens, to four O(2) at $(\frac{1}{2}, \frac{1}{2}, z)$ sites, and to one O(2) at a $(0, 0, z)$ site.

C. Charge Distribution

Figure 7.23 shows contours of constant-valence charge density on a logarithmic scale drawn on the back x, z -plane and on the diagonal plane of the unit cell sketched in Fig. 7.13. These contour plots are obtained from the band structure calculations described in Chapter 8, Section XIV. The high-charge density at the lanthanum site and the low charge density around this site indicate an ionic state

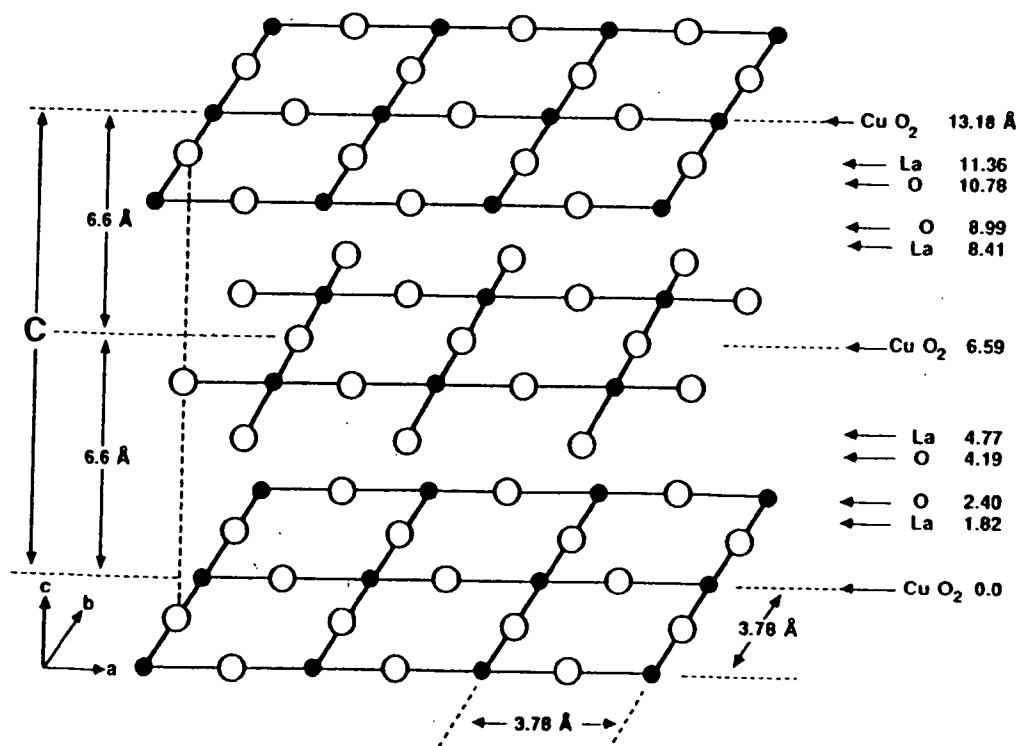


Figure 7.21 CuO_2 layers of the La_2CuO_4 structure showing horizontal displacement of Cu atoms in alternate layers. The layers are perpendicular to the c -axis (Poole *et al.*, 1988, p. 87).

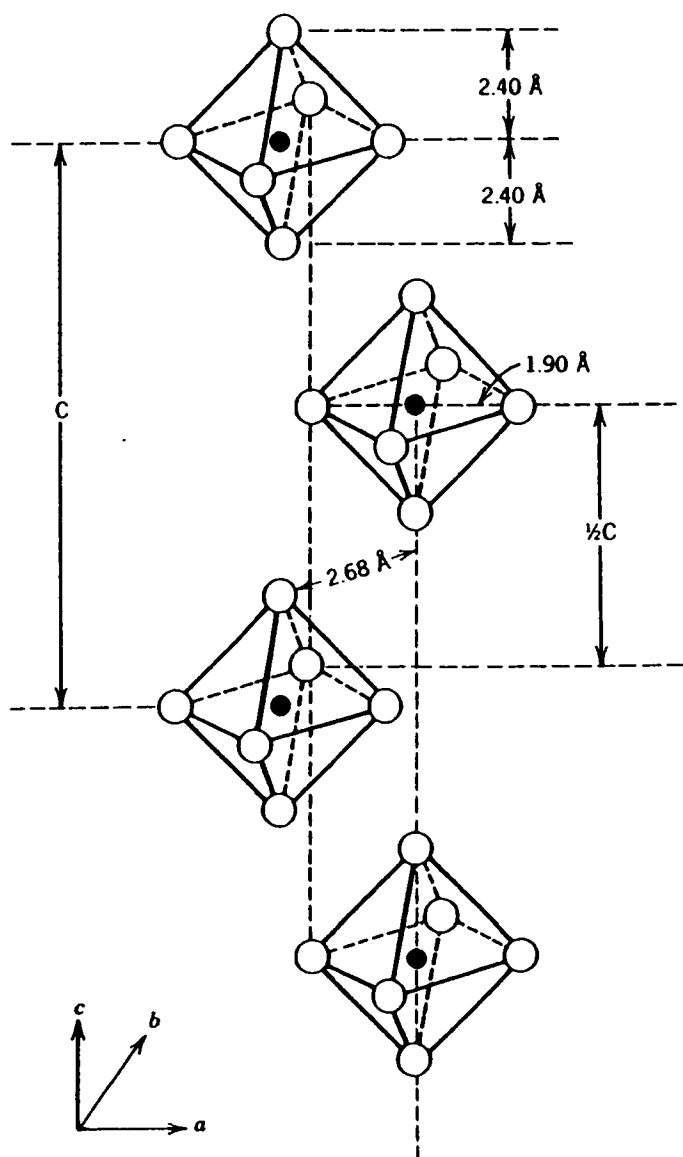


Figure 7.22 Ordering of axially distorted CuO_6 octahedra in La_2CuO_4 (Poole *et al.*, 1988, p. 88).

La^{3+} . The charge density changes in a fairly regular manner around the copper and oxygen atoms, both within the CuO_2 planes and perpendicular to these planes, suggestive of covalency in the Cu–O bonding, as is the case with the $\text{YBa}_2\text{Cu}_3\text{O}_7$ compound.

D. Superconducting Structures

The compound La_2CuO_4 is itself an antiferromagnetic insulator and must be doped, generally with an alkaline earth, to exhibit pronounced superconducting prop-

erties. The compounds $(\text{La}_{1-x}\text{M}_x)_2\text{CuO}_4$, with 3% to 15% of $M = \text{Sr}$ or Ba replacing La , are orthorhombic at low temperatures and low M contents and are tetragonal otherwise; superconductivity has been found on both sides of this transition. The orthorhombic distortion can be of the rectangular or of the rhombal type, both of which are sketched in Fig. 7.4. The phase diagram of Fig. 7.24 shows the tetragonal, orthorhombic, superconducting, and antiferromagnetically ordered regions for the lanthanum compound (Weber *et al.*, 1989; cf. Goodenough *et al.*, 1993). We see that

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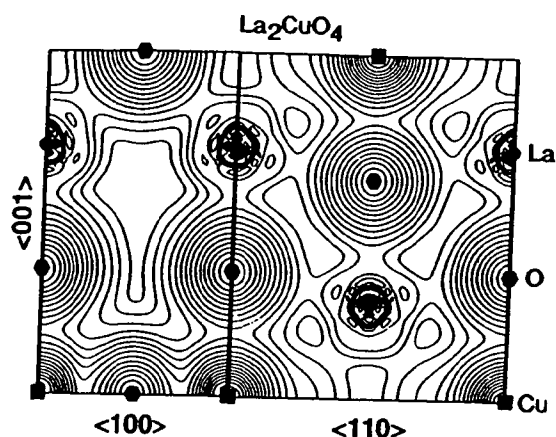


Figure 7.23 Contour plots of the charge density of La_2CuO_4 obtained from band structure calculations. The x, z -crystallographic plane labeled $\langle 100 \rangle$ is shown on the left and the diagonal plane labeled $\langle 110 \rangle$ on the right. The contour spacing is on a logarithmic scale (Pickett, 1989).

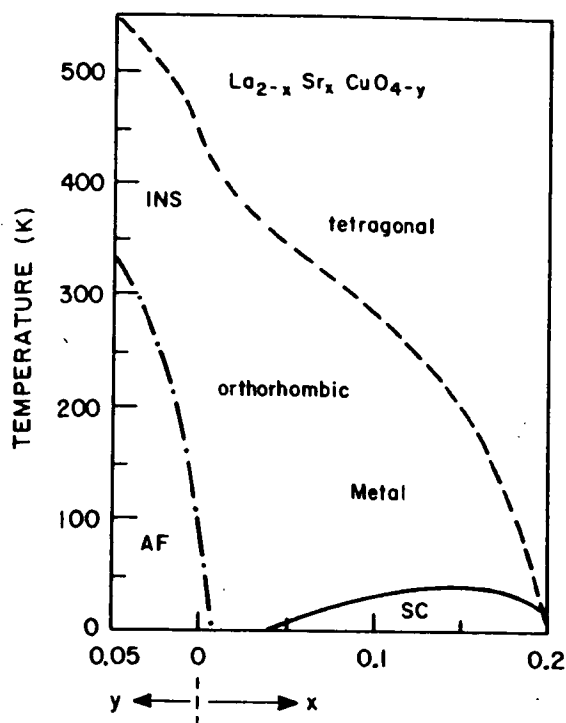


Figure 7.24 Phase diagram for hole-type $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ indicating insulating (INS), antiferromagnetic (AF), and superconducting (SC) regions. Figure VI-6 of Poole *et al.* (1988) shows experimental data along the orthorhombic-to-tetragonal transition line. Spin-density waves (SDW) are found in the AF region (Weber *et al.*, 1989).

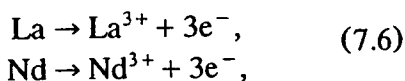
the orthorhombic phase is insulating at high temperatures, metallic at low temperatures, and superconducting at very low temperatures. Spin-density waves, to be discussed in Chapter 8, Section XIX, occur in the antiferromagnetic region.

E. Nd_2CuO_4 Compound (T' Phase)

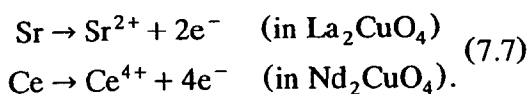
The rarer Nd_2CuO_4 structure (Skanakumar *et al.*, 1989; Sulewski *et al.*, 1990; Tan *et al.*, 1990) given on the right side of Fig. 7.18 and Table 7.5 has all of its atoms in the same positions as the standard La_2CuO_4 structure, except for the apical O(2) oxygens in the [O-La] and [La-O] layers, which move to form a $[-\text{O}_2-]$ layer between $[-\text{La}]$ and $[\text{La}-]$. These oxygens, now called O(3), have the same x, y coordinate positions as the O(1) oxygens, and are located exactly between the CuO_2 planes with $z = \frac{1}{4}$ or $\frac{3}{4}$. We see from Fig. 7.18 that the CuO_6 octahedra have now lost their apical oxygens, causing Cu to become square planar-coordinated CuO_4 groups. The Nd is eightfold coordinated to four O(1) and four O(3) atoms, but with slightly different Nd-O distances. The CuO_2 planes, however, are identical in the two structures. Superconductors with this Nd_2CuO_4 structure are of the electron type, in contrast to other high-temperature superconductors, in which the current carriers are holes. In particular, the electron superconductor $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ with $T_c = 24$ K has been widely studied (Fontcuberta and Fàbrega, 1995, a review chapter; Allen 1990; Alp *et al.*, 1989b; Barlingay *et al.*, 1990; Ekino and Akimitsu, 1989a, b; Lederman *et al.*, 1991; Luke *et al.*, 1990; Lynn *et al.*, 1990; Sugiyama *et al.*, 1991; Tarason *et al.*, 1989a). Other rare earths, such as Pr (Lee *et al.*, 1990) and Sm (Almasan *et al.*, 1992) have replaced Nd.

The difference of structures associated with different signs attached to the current carriers may be understood in terms of the doping process that converts undoped material into a superconductor. Lanthanum and neodymium are both trivalent, and in the undoped compounds they each con-

tribute three electrons to the nearby oxygens,



to produce O^{2-} . To form the superconductors a small amount of La in La_2CuO_4 can be replaced with divalent Sr, and some Nd in Nd_2CuO_4 can be replaced with tetravalent Ce, corresponding to



Thus, Sr doping decreases the number of electrons to produce hole-type carriers, while Ce doping increases the electron concentration and the conductivity is electron type.

There are also copper-oxide electron superconductors with different structures, such as $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$ (Smith *et al.*, 1991) and $\text{TlCa}_{1-x}R_x\text{Sr}_2\text{Cu}_2\text{O}_{7-\delta}$, where R is a rare earth (Vijayaraghavan *et al.*, 1989). Electron- and hole-type superconductivity in the cuprates has been compared (Katti and Risbud, 1992; Medina and Regueiro, 1990).

F. $\text{La}_{2-x-y}\text{R}_x\text{Sr}_y\text{CuO}_4$ Compounds (T* Phase)

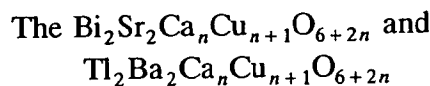
We have described the T structure of La_2CuO_4 and the T' structure of Nd_2CuO_4 . The former has O(2) oxygens and the latter O(3) oxygens, which changes the coordinations of the Cu atoms and that of the La and Nd atoms as well. There is a hybrid structure of hole-type superconducting lanthanum cuprates called the T* structure, illustrated in Fig. 7.18b, in which the upper half of the unit cell is the T type with O(2) oxygens and lower half the T' type with O(3) oxygens. These two varieties of halfcells are stacked alternately along the tetragonal c -axis (Akimitsu *et al.*, 1988; Cheong *et al.*, 1989b; Kwei *et al.*, 1990; Tan *et al.*, 1990). Copper, located in the base of an oxygen pyramid, is fivefold-coordinated CuO_5 . There are two inequivalent rare earth sites; the ninefold-coordinated site in the T-type halfcell is

preferentially occupied by the larger La and Sr ions, while the smaller rare earths R (i.e., Sm, Eu, Gd, or Tb) prefer the eightfold-coordinated site in the T' half-cell. Tan *et al.* (1991) give a phase diagram for the concentration ranges over which the T and T* phases are predominant.

IX. BODY-CENTERED BiSrCaCuO AND TlBaCaCuO

Early in 1988 two new superconducting systems with transition temperatures considerably above those attainable with YBaCuO , namely the bismuth- and thallium-based materials, were discovered. These compounds have about the same a and b lattice constants as the yttrium and lanthanum compounds, but with much larger unit cell dimensions along c . We will describe their body-centered structures in terms of their layering schemes. In the late 1940s some related compounds were synthesized by the Swedish chemist Bengt Aurivillius (1950, 1951, 1952).

A. Layering Scheme



compounds, where n is an integer, have essentially the same structure and the same layering arrangement (Barry *et al.*, 1989; Siegrist *et al.*, 1988; Torardi *et al.*, 1988a; Yvon and François, 1989), although there are some differences in the detailed atom positions. Here there are groupings of CuO_2 layers, each separated from the next by Ca layers with no oxygen. The CuO_2 groupings are bound together by intervening layers of BiO and SrO for the bismuth compound, and by intervening layers of TlO and BaO for the thallium compound. Figure 7.25 compares the layering scheme of the $\text{Tl}_2\text{Ba}_2\text{Ca}_n\text{Cu}_{n+1}\text{O}_{6+2n}$ compounds with $n = 0, 1, 2$ with those of the lanthanum and yttrium compounds. We also see from the figure that the groupings of $[\text{Cu O}_2 -]$ planes and $[- \text{O}_2 \text{ Cu}]$ image

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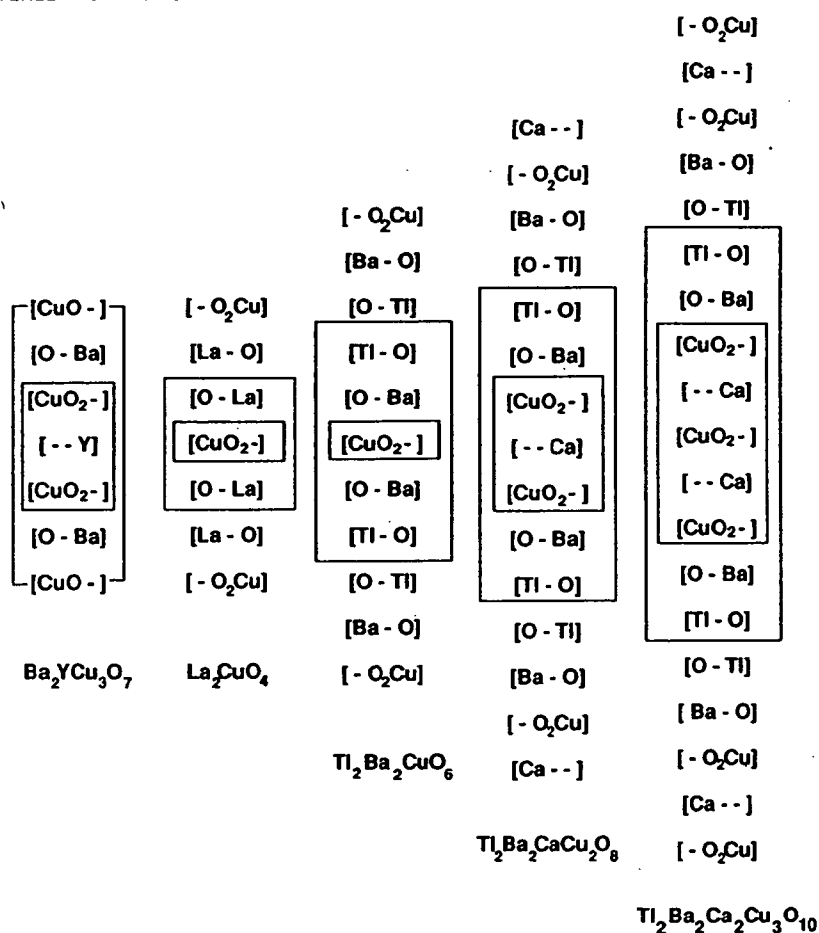


Figure 7.25 Layering schemes of various high-temperature superconductors. The CuO_2 plane layers are enclosed in small inner boxes, and the layers that make up a formula unit are enclosed in larger boxes. The Bi-Sr compounds $Bi_2Sr_2Ca_nCu_{n+1}O_{6+2n}$ have the same layering schemes as their Tl-Ba counterparts shown in this figure.

(i.e., body centered) planes repeat along the c -axis. It is these copper-oxide layers that are responsible for the superconducting properties.

A close examination of this figure shows that the general stacking rules mentioned in Section VI.C for the layering scheme are satisfied, namely metal ions in adjacent layers alternate between edge (E) and centered (C) sites, and adjacent layers never have oxygens on the same types of sites. The horizontal reflection symmetry at the central point of the cell is evident. It is also clear that $YBa_2Cu_3O_7$ is aligned and that the other four compounds are staggered.

Figure 7.26 (Torardi *et al.*, 1988a) presents a more graphical representation of the information in Fig. 7.25 by showing the

positions of the atoms in their layers. The symmetry and body centering rules are also evident on this figure. Rao (1991) provided sketches for the six compounds $Tl_mBa_2Ca_nCu_{n+1}O_x$ similar to those in Fig. 7.26 with the compound containing one ($m = 1$) or two thallium layers ($m = 2$), where $n = 0, 1, 2$, as in the Torardi *et al.* figure.

B. Nomenclature

There are always two thalliums and two bariums in the basic formula for $Tl_2Ba_2Ca_nCu_{n+1}O_{6+2n}$, together with n calciums and $n + 1$ coppers. The first three members of this series for $n = 0, 1$, and 2 are called the 2201, 2212, and 2223 compounds, respectively, and similarly for their

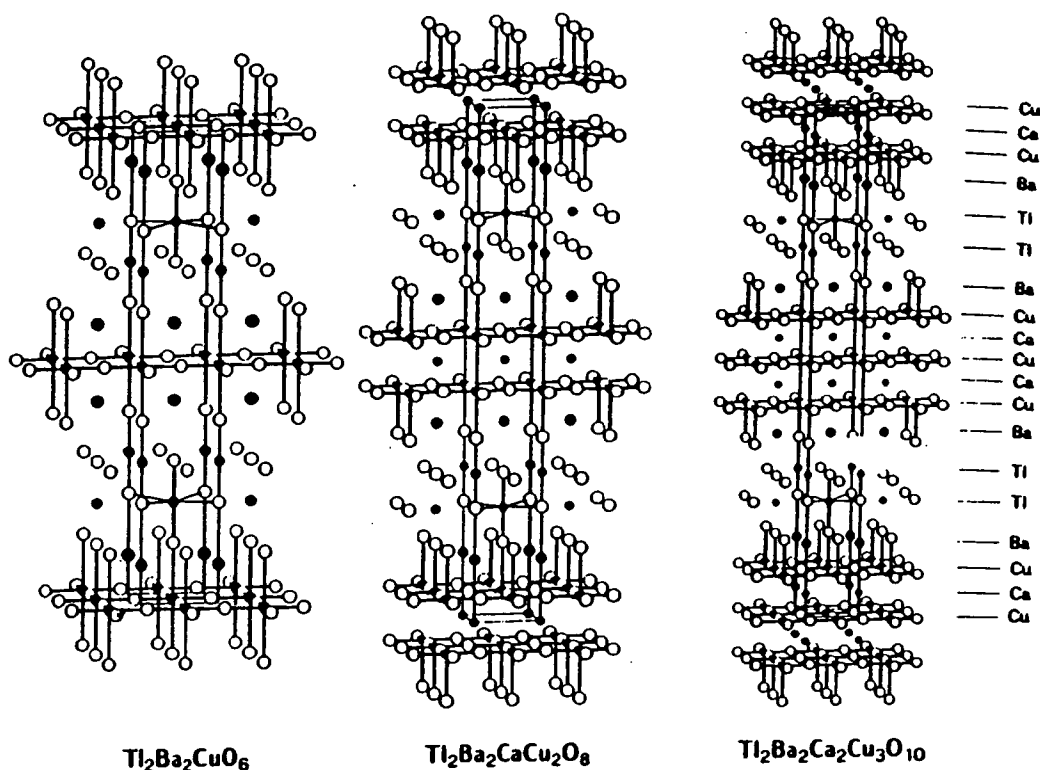


Figure 7.26 Crystal structures of $\text{Tl}_2\text{Ba}_2\text{Ca}_n\text{Cu}_{n+1}\text{O}_{6+2n}$ superconducting compounds with $n = 0, 1, 2$ arranged to display the layering schemes. The $\text{Bi}_2\text{Sr}_2\text{Ca}_n\text{Cu}_{n+1}\text{O}_{6+2n}$ compounds have the same respective structures (Torardi *et al.*, 1988a).

BiSr analogues $\text{Bi}_2\text{Sr}_2\text{Ca}_n\text{Cu}_{n+1}\text{O}_{6+2n}$. Since Y in $\text{YBa}_2\text{Cu}_3\text{O}_7$ is structurally analogous to Ca in the Tl and Bi compounds, it would be more consistent to write $\text{Ba}_2\text{YCu}_3\text{O}_7$ for its formula, as noted in Section VI.F. In this spirit $\text{Ba}_2\text{YCu}_3\text{O}_{7-\delta}$ might be called the 0213 compound, and $(\text{La}_{1-x}\text{M}_x)_2\text{CuO}_{4-\delta}$ could be called 2001.

C. Bi-Sr Compounds

Now that the overall structures and interrelationships of the BiSr and TlBa high-temperature superconductors have been made clear in Figs. 7.25 and 7.26 we will comment briefly about each compound. Table 7.3 summarizes the characteristics of these and related compounds.

The first member of the BiSr series, the 2201 compound with $n = 0$, has octahedrally coordinated Cu and $T_c \approx 9$ K (Torardi *et al.*, 1988b). The second mem-

ber, $\text{Bi}_2(\text{Sr}, \text{Ca})_3\text{Cu}_2\text{O}_{8+\delta}$, is a superconductor with $T_c \approx 90$ K (Subramanian *et al.*, 1988a; Tarascon *et al.*, 1988b). There are two $[\text{Cu O}_2 -]$ layers separated from each other by the $[- - \text{Ca}]$ layer. The spacing from $[\text{Cu O}_2 -]$ to $[- - \text{Ca}]$ is 1.66 Å, which is less than the corresponding spacing of 1.99 Å between the levels $[\text{Cu O}_2 -]$ and $[- - \text{Y}]$ of YBaCuO . In both cases the copper ions have a pyramidal oxygen coordination of the type shown in Fig. 7.11. Superlattice structures have been reported along a and b , which means that minor modifications of the unit cells repeat approximately every five lattice spacings, as explained in Sect. IX.E. The third member of the series, $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, has three CuO_2 layers separated from each other by $[- - \text{Ca}]$ planes and a higher transition temperature, 110 K, when doped with Pb. The two Cu ions have pyramidal coordination, while the third is square planar.

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indicate the same type of covalency in the Cu-O bonding as with the $\text{YBa}_2\text{Cu}_3\text{O}_7$ and La_2CuO_4 compounds. They also indicate very little bonding between the adjacent [Bi - O] and [O - Bi] layers.

D. Tl-Ba Compounds

The TlBa compounds



have higher transition temperatures than their bismuth counterparts (Iqbal *et al.*, 1989; Subramanian *et al.*, 1988b; Torardi *et al.*, 1988a). The first member of the series, namely $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ with $n = 0$, has no [- - Ca] layer and a relatively low transition temperature of ≈ 85 K. The second member ($n = 1$), $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$, called the 2212 compound, with $T_c = 110$ K

has the same layering scheme as its Bi counterpart, detailed in Figs. 7.25 and 7.26. The $[\text{Cu O}_2 -]$ layers are thicker and closer together than the corresponding layers of the bismuth compound (Toby *et al.*, 1990). The third member of the series, $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, has three $[\text{Cu O}_2 -]$ layers separated from each other by [- - Ca] planes, and the highest transition temperature, 125 K, of this series of thallium compounds. It has the same copper coordination as its BiSr counterpart. The 2212 and 2223 compounds are tetragonal and belong to the same crystallographic space group as La_2CuO_4 .

We see from the charge-density plot of $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ shown in Fig. 7.27 that Ba^{2+} is ionic, Cu exhibits strong covalency, especially in the Cu-O plane, and Tl also appears to have a pronounced covalency. The bonding between the [Tl - O] and [O - Tl] planes is stronger than that between the [Bi - O] and [O - Bi] planes of Bi-Sr.

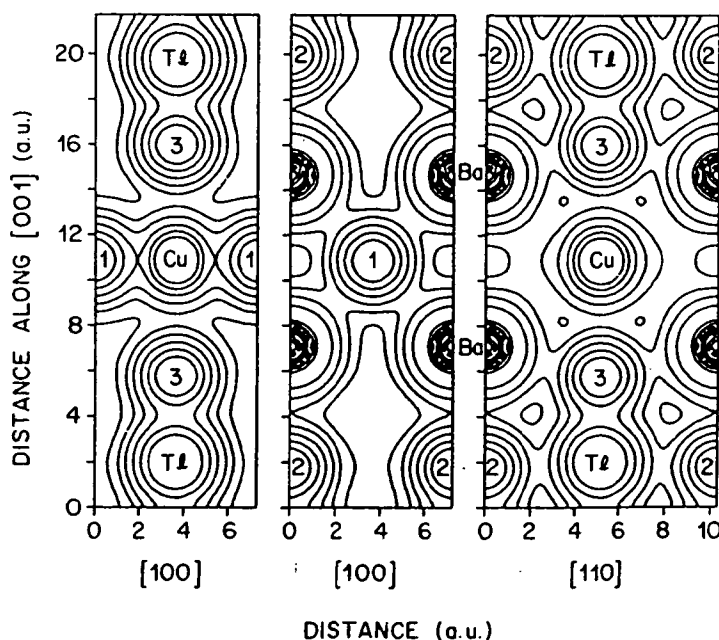
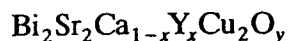


Figure 7.27 Contours of constant charge density on a logarithmic scale in two high-symmetry crystallographic planes of $\text{Tl}_2\text{Ba}_2\text{CuO}_6$. Oxygen atoms O(1), O(2), and O(3) are denoted 1, 2, and 3, respectively. The planar Cu-O1 binding is strongest (Hamann and Mattheiss, 1988; see Pickett, 1989).

E. Modulated Structures

The x-ray and neutron-diffraction patterns obtained during crystal structure determinations of the bismuth cuprates $\text{Bi}_2\text{Sr}_2\text{Ca}_n\text{Cu}_{n+1}\text{O}_{6+2n}$ exhibit weak satellite lines with spacings that do not arise from an integral multiple of the unit cell dimensions. These satellites have modulation periods of 21 Å, 19.6 Å, and 20.8 Å, respectively, for the $n = 0, 1$, and 2 compounds (Li *et al.*, 1989). Since the lattice constant $a = 5.41$ Å ($b = 5.43$ Å) for all three compounds, this corresponds to a superlattice with unit cell of dimensions $\approx 3.8a, b, c$, with the repeat unit along the a direction equal to $\approx 3.8a$ for all three compounds. A modulation of $4.7b$ has also been reported (Kulik *et al.*, 1990). This structural modulation is called incommensurate because the repeat unit is not an integral multiple of a .

Substitutions dramatically change this modulation. The compound



has a period that decreases from about $4.8b$ for $x = 0$ to the commensurate value $4.0b$ for $x = 1$ (Inoue *et al.*, 1989; Tamegai *et al.*, 1989). Replacing Cu by a transition metal (Fe, Mn, or Co) produces nonsuperconducting compounds with a structural modulation that is commensurate with the lattice spacing (Tarascon *et al.*, 1989b). A modulation-free bismuth-lead cuprate superconductor has been prepared (Manivannan *et al.*, 1991). Kistenmacher (1989) examined substitution-induced superstructures in $\text{YBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_7$. Superlattices with modulation wavelengths as short as 24 Å have been prepared by employing ultra-thin deposition techniques to interpose insulating planes of $\text{PrBa}_2\text{Cu}_3\text{O}_7$ between superconducting Cu-O layers of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Jakob *et al.*, 1991; Lowndes *et al.*, 1990; Pennycook *et al.*, 1991; Rajagopal and Mahanti, 1991; Triscone *et al.*, 1990). Tanaka and Tsukada (1991) used the Kronig-Penney model (Tanaka and

Tsukada, 1989a,b) to calculate the quasi-particle spectrum of superlattices.

F. Aligned Tl-Ba Compounds

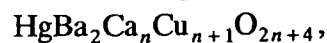
A series of aligned thallium-based superconducting compounds that have the general formula $\text{TlBa}_2\text{Ca}_n\text{Cu}_{n+1}\text{O}_{5+2n}$ with n varying from 0 to 5 has been reported (Ihara *et al.*, 1988; Rona, 1990). These constitute a series from 1201 to 1245. They have superconducting transition temperatures almost as high as the $\text{Tl}_2\text{Ba}_2\text{Ca}_n\text{Cu}_{n+1}\text{O}_{6+2n}$ compounds. Data on these compounds are listed in Table 7.3.

G. Lead Doping

In recent years a great deal of effort has been expended in synthesizing lead-doped superconducting cuprate structures (Itoh and Uchikawa, 1989). Examples involve substituting Pb for Bi (Dou *et al.*, 1989; Zhengping *et al.*, 1990), for Tl (Barry *et al.*, 1989; Mingzhu *et al.*, 1990), or for both Bi and Tl (Iqbal *et al.*, 1990). Different kinds of Pb, Y-containing superconductors have also been prepared (cf. Mattheiss and Hamann, 1989; Ohta and Maekawa, 1990; Tang *et al.*, 1991; Tokiwa *et al.*, 1990, 1991).

X. ALIGNED HgBaCaCuO

The series of compounds



where n is an integer, are prototypes for the Hg family of superconductors. The first three members of the family, with $n = 0, 1, 2$, are often referred to as Hg-1201, Hg-1212, and Hg-1223, respectively. They have the structures sketched in Fig. 7.28 (Tokiwa-Yamamoto *et al.*, 1993; see also Martin *et al.*, 1994; Putilin *et al.*, 1991). The lattice constants are $a = 3.86$ Å for all of them, and $c = 9.5, 12.6$, and 15.7 Å for $n = 0, 1, 2$, respectively. The atom positions of the $n = 1$ compound are listed in Table 7.6 (Hur *et al.*, 1994). The figure is drawn

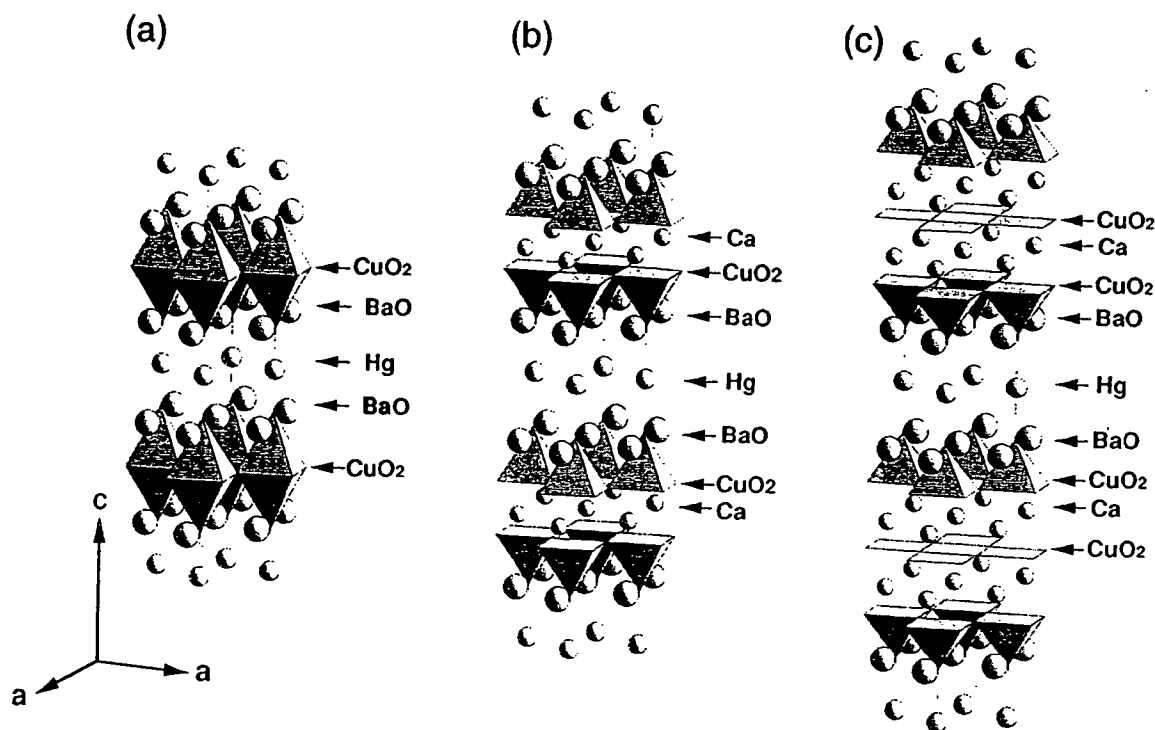


Figure 7.28 Structural models for the series $\text{HgBa}_2\text{Ca}_n\text{Cu}_{n+1}\text{O}_{2n+4}$. The first three members with $n = 0, 1, 2$ are shown (parts a, b, and c, respectively) (Tokiwa-Yamamoto *et al.*, 1993).

Table 7.6 Normalized Atom Positions in the Tetragonal Unit Cell of $\text{HgBa}_2\text{Ca}_{0.86}\text{Sr}_{0.14}\text{Cu}_2\text{O}_{6+\delta}$ ^a

Layer	Atom	<i>x</i>	<i>y</i>	<i>z</i>
[Hg - -]	Hg	0	0	1
	O(3)	$\frac{1}{2}$	$\frac{1}{2}$	1
	O(2)	0	0	0.843
[O - Ba]	Ba	$\frac{1}{2}$	$\frac{1}{2}$	0.778
	Cu	0	0	0.621
[Cu O ₂ -]	O(1)	0	$\frac{1}{2}$	0.627
	O(1)	$\frac{1}{2}$	0	0.627
[- - Ca]	Ca, Sr	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
	O(1)	$\frac{1}{2}$	0	0.373
[Cu O ₂ -]	O(1)	0	$\frac{1}{2}$	0.373
	Cu	0	0	0.379
	Ba	$\frac{1}{2}$	$\frac{1}{2}$	0.222
[O - Ba]	O(2)	0	0	0.157
	O(3)	$\frac{1}{2}$	$\frac{1}{2}$	0
[Hg - -]	Hg	0	0	0

^a Unit cell dimensions $a = 3.8584 \text{ \AA}$ and $c = 12.6646 \text{ \AA}$, space group is $P4/mmm$, D_{4h}^1 . The Hg site is 91% occupied and the O(3) site is 11% occupied ($\delta = 0.11$). The data are from Hur *et al.* (1994).

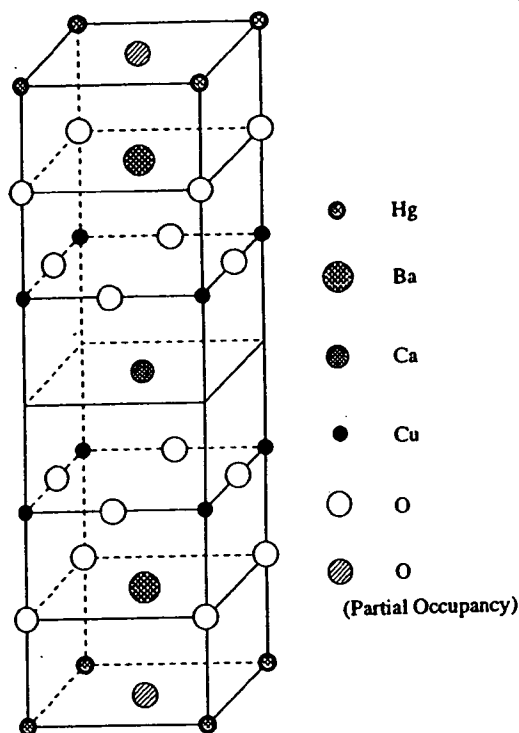


Figure 7.29 Schematic structure of the $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$ compound which is also called Hg-1212 (Meng *et al.*, 1993a).

with mercury located in the middle layer of the unit cell, while the table puts Hg at the origin (000) and Ca in the middle ($\frac{1}{2} \frac{1}{2} \frac{1}{2}$). Figure 7.29 presents the unit cell for the $n = 1$ compound $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$ drawn with Ca in the middle (Meng *et al.*, 1993a). The symbol δ represents a small excess of oxygen located in the center of the top and bottom layers, at positions $\frac{1}{2} \frac{1}{2} 0$ and $\frac{1}{2} \frac{1}{2} 1$ which are labeled "partial occupancy" in the figure. If this oxygen were included the level symbol would be [Hg - O] instead of [Hg - -]. These Hg compound structures are similar to those of the series $\text{TlBa}_2\text{Ca}_n\text{Cu}_{n+1}\text{O}_{2n+4}$ mentioned above in Section IX.F.

We see from Fig. 7.28 that the copper atom of Hg-1201 is in the center of a stretched octahedron with the planar oxygens O(1) at a distance of 1.94 Å, and the apical oxygens O(2) of the [O - Ba] layer much further away (2.78 Å). For $n = 1$ each copper atom is in the center of the

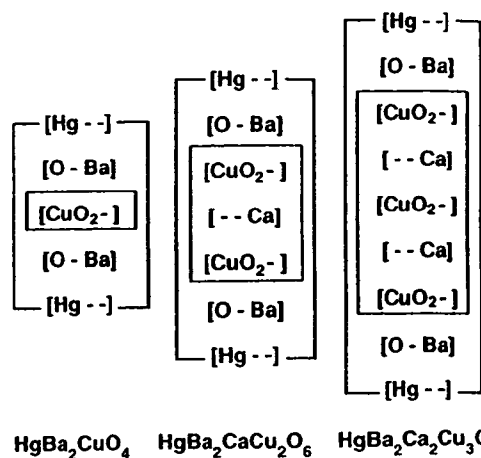
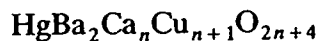


Figure 7.30 Layering schemes of three $\text{HgBa}_2\text{Ca}_n\text{Cu}_{n+1}\text{O}_{2n+4}$ compounds, using the notation of Fig. 7.25.

base of a tetragonal pyramid, and for $n = 2$ the additional CuO_2 layer has Cu atoms which are square planar coordinated. The layering scheme stacking rules of Section VI.C are obeyed by the Hg series of compounds, with metal ions in adjacent layers alternating between edge (E) and centered (C) sites, and oxygen in adjacent layers always at different sites. We see from Table 7.6 that the [O - Ba] layer is strongly puckered and the $[\text{Cu O}_2 -]$ layer is only slightly puckered.

The relationships between the layering scheme of the $\text{HgBa}_2\text{Ca}_n\text{Cu}_{n+1}\text{O}_{2n+4}$ series of compounds and those of the other cuprates may be seen by comparing the sketch of Fig. 7.30 with that of Fig. 7.25. We see that the $n = 1$ compound $\text{HgBa}_2\text{CaCu}_2\text{O}_6$ is quite similar in structure to $\text{YBa}_2\text{Cu}_3\text{O}_7$ with Ca replacing Y in the center and Hg replacing the chains $[\text{Cu O} -]$. More surprising is the similarity between the arrangement of the atoms in the unit cell of each



compound and the arrangement of the atoms in the semi-unit cell of the corresponding



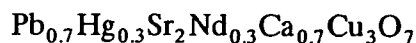
compound. They are the same except for the replacement of the [Ti - O] layer by [Hg - -], and the fact that the thallium compounds are body centered and the Hg ones are aligned.

Supercells involving polytypes with ordered stacking sequences of different phases, such as Hg-1212 and Hg-1223, along the *c* direction have been reported. The stoichiometry is often



corresponding to equal numbers of the Hg-1212 and Hg-1223 phases (Phillips, 1993; Schilling *et al.*, 1993, 1994).

Detailed structural data have already been reported on various Hg family compounds such as $\text{HgBa}_2\text{CuO}_{4+\delta}$ (Putlin *et al.*, 1993) and the $n = 1$ compound with partial Eu substitution for Ca (Putlin *et al.*, 1991). The compound



has Hg in the position (0.065, 0, 0), slightly displaced from the origin of the unit cell (Martin *et al.*, 1994). Several researchers have reported synthesis and pretreatment procedures (Adachi *et al.*, 1993; Itoh *et al.*, 1993; Isawa 1994a; Meng, 1993b; Paranthaman, 1994; Paranthaman *et al.*, 1993). Lead doping for Hg has been used to improve the superconducting properties (Iqbal *et al.*, 1994; Isawa *et al.*, 1993; Martin *et al.*, 1994).

XI. BUCKMINSTERFULLERENES

The compound C_{60} , called buckminsterfullerene, or fullerene for short, con-

sists of 60 carbon atoms at the vertices of the dotriacontahedron (32-sided figure) that is sketched in Fig. 3.35 and discussed in Chapter 3, Section XVI. The term fullerene is used here for a wider class of compounds C_n with n carbon atoms, each of whose carbon atoms is bonded to three other carbons to form a closed surface, with the system conjugated such that for every resonant structure each carbon has two single bonds and one double bond. The smallest possible compound of this type is tetrahedral C_4 , which has the three resonant structures shown in Fig. 7.31. Cubic C_8 is a fullerene, and we show in Problem 17 that it has nine resonant structures. Icosahedral C_{12} is also a fullerene, but octahedral C_6 and dodecahedral C_{20} are not because their carbons are bonded to more than three neighbors. These hypothetical smaller C_n compounds have never been synthesized, but the larger ones, such as C_{60} , C_{70} , C_{76} , C_{78} , and C_{82} , have been made and characterized. Some of them have several forms, with different arrangements of polygons. Clusters of buckminsterfullerenes, such as icosahedral $(\text{C}_{60})_{13}$, have also been studied (T. P. Martin *et al.*, 1993).

There are several interesting geometrical characteristics of fullerenes (Chung and Sternberg, 1993). Since each carbon (vertex) joins three bonds (edges) and each edge has two vertices, the number of edges E in a structure C_n is 50% greater than the number of vertices V . There is a general theorem in topology, called Euler's Theorem, that the number of faces F of a

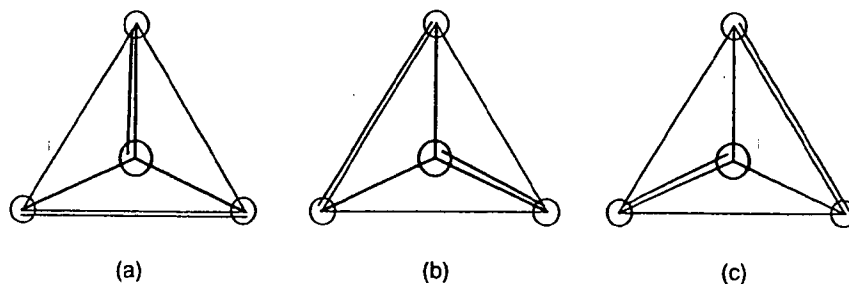


Figure 7.31 The three resonant structures of the (hypothetical) tetrahedral compound C_4 .

polyhedron is given by the formula

$$F = E - V + 2. \quad (7.8)$$

In a fullerene C_n where $n = V$ three edges meet at each vertex, so we have

$$E = 3V/2, \quad (7.9)$$

$$F = \frac{V}{2} + 2. \quad (7.10)$$

It is shown in Problem 16 that

$$E = \frac{1}{2} \sum_s sF_s, \quad (7.11a)$$

$$V = \frac{1}{3} \sum_s sF_s, \quad (7.11b)$$

where F_s is the number of faces with s sides, and of course,

$$F = \sum_s F_s. \quad (7.12)$$

Combining Eqs. (7.10)–(7.12) gives the fullerene face formula

$$\sum_s (6 - s)F_s = 12. \quad (7.13)$$

This expression does not place any restrictions on the number of hexagons (F_6), but it does severely limit the number of other polyhedra. The two smallest hypothetical fullerenes, the tetrahedron and the cube, have no hexagons, and the larger ones consist of 12 pentagons (F_5), from Eq. (7.13), and numerous hexagons. For example, the molecule C_{60} with $V = 60$ has 12 pentagons and 20 hexagons. Table 7.7 gives the geometric characteristics of the five Platonic solids, the solids generated by truncating all of their vertices, and several other regular polygons, most of which are fullerenes. The fullerenes of current interest are C_{60} and larger molecules consisting of 12 pentagons and numerous hexagons, such as C_{70} , C_{76} , C_{78} , and C_{82} . Some have several varieties, such as the isomers of C_{78} with the symmetries C_{2v} , D_3 , and D_{3h} (Diederich and Whetten, 1992).

The outer diameter of the C_{60} molecule is 7.10 Å and its van der Waals separation is 2.9 Å, so that the nearest-neighbor distance (effective diameter) in a

Table 7.7 Characteristics of Several Regular Solids^a

Figure	Vertices	Edges	Faces	Face (polygon) type
Tetrahedron	4	6	4	all equilateral triangles
Octahedron ^b	6	12	8	all equilateral triangles
Cube	8	12	6	all squares
Icosahedron ^b	12	30	20	all equilateral triangles
Dodecahedron (pentagonal)	20	30	12	all regular pentagons
Hexadecahedron	28	42	16	12 pentagons, 4 hexagons
Truncated tetrahedron	12	18	8	4 equilateral triangles, 4 hexagons
Truncated octahedron	24	36	14	6 squares, 8 hexagons
Truncated cube	24	36	14	8 equilateral triangles, 6 octagons
Dotriacontohedron (truncated icosahedron)	60	90	32	12 regular pentagons, 20 hexagons
Truncated dodecahedron	60	90	32	20 equilateral triangles, 12 decagons
Heptatriacontohedron	70	105	37	12 pentagons (2 regular), 25 hexagons
Tetracontahedron	76	114	40	12 pentagons, 28 hexagons
Hentetracontohedron	78	116	41	12 pentagons, 29 hexagons
Dotetracontohedron	84	126	44	12 pentagons, 32 hexagons
Large Fullerene	n	$\frac{3}{2}n$	$\frac{1}{2}n + 2$	12 pentagons, $\frac{1}{2}n - 10$ hexagons

^a The first five solids are the Platonic solids, and the seventh to eleventh are truncations of the Platonic solids. When carbons occupy the vertices all correspond to fullerenes except the octahedron and the icosahedron for which $3V \neq 2E$. The smallest compounds in this table have never been synthesized.

^b Not a fullerene because the vertices have more than three edges.

solid is 10.0 Å. The bonds shared by a five-membered and a six-membered ring are 1.45 Å long, while those between two adjacent six-membered rings are 1.40 Å long. Above 260 K these molecules form a face centered cubic lattice with lattice constant 14.2 Å; below 260 K it is simple cubic with $a = 7.10$ Å (Fischer *et al.*, 1991; Kasatani *et al.*, 1993; Troullier and Martins, 1992). When C_{60} is doped with alkali metals to form a superconductor it crystallizes into a face centered cubic lattice with larger octahedral and smaller tetrahedral holes for the alkalis. The C_{60} ions are orientationally disordered in the lattice (Gupta and Gupta, 1993).

XII. SYMMETRIES

Earlier in this chapter we mentioned the significance of the horizontal reflection plane σ_h characteristic of the high-temperature superconductors, and noted that most of these superconductors are body centered. In this section we will point out additional symmetries that are present. Table VI-14 of our earlier work (Poole *et al.*, 1988) lists the point symmetries at the sites of the atoms in a number of these compounds.

In the notation of group theory the tetragonal structure belongs to the point group $4/mmm$ (this is the newer international notation for what in the older Schönflies notation was written D_{4h}). The unit cell possesses the inversion operation at the center, so when there is an atom at position (x, y, z) , there will be another identical atom at position $(-x, -y, -z)$. The international symbol $4/mmm$ indicates the presence of a fourfold axis of symmetry C_4 and three mutually perpendicular mirror planes m . The Schönflies notation D_{4h} also specifies the fourfold axis, h signifying a horizontal mirror plane σ_h and D indicating a dihedral group with vertical mirror planes.

We see from Fig. 7.32 that the z -axis is a fourfold (90°) symmetry axis called C_4 , and that perpendicular to it are twofold (180°) symmetry axes along the x and y directions, called C_2 , and also along the diagonal directions (C'_2) in the midplane. There are two vertical mirror planes σ_v , two diagonal mirror planes σ_d which are also vertical, and a horizontal mirror plane σ_h . Additional symmetry operations that are not shown are a 180° rotation C_2^z around the z axis,

$$C_2^z = C_4^z C_4^z, \quad (7.14)$$

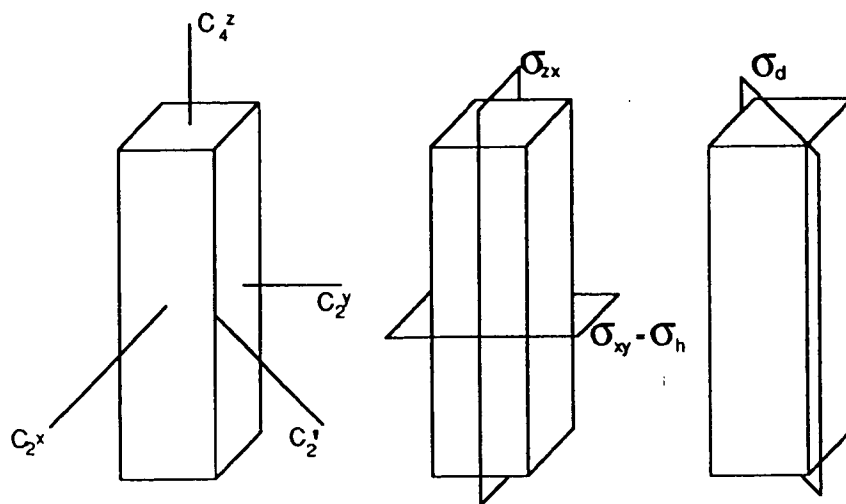


Figure 7.32 Symmetry operations of the tetragonal unit cell showing a fourfold rotation axis C_4 , three twofold axes C_2 , and reflection planes of the vertical $\sigma_{zx} = \sigma_v$, horizontal $\sigma_{xy} = \sigma_h$, and diagonal σ_d types.

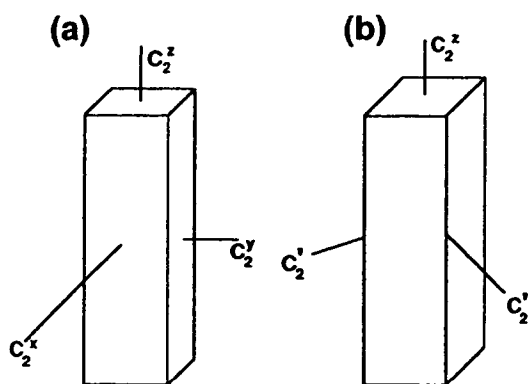


Figure 7.33 Rotational symmetry operations of an orthorhombic unit cell (a) with rectangular distortion, and (b) with rhombal distortion from an originally tetragonal cell.

and the improper fourfold rotation S_4^z around z that corresponds to C_4^z followed by, or preceded by, σ_h ,

$$S_4^z = C_4^z \sigma_h = \sigma_h C_4^z, \quad (7.15)$$

where C_4^z and σ_h commute.

The orthorhombic structure has mmm , D_{2h} symmetry. We see from Fig. 7.33 that both the rectangular and rhombal unit cells, which correspond to Figs. 7.4a and 7.4b, respectively, have three mutually perpendicular twofold axes, and that they also have three mutually perpendicular mirror planes σ , which are not shown. The two cases differ in having their horizontal axes and vertical planes oriented at 45° to each other.

Cubic structures, being much higher in symmetry, have additional symmetry operations, such as fourfold axes C_4^x , C_4^y , and C_4^z along each coordinate direction, threefold axes C_3 along each body diagonal, and numerous other mirror planes. These can be easily seen from an examination of Fig. 7.1. Buckyballs belong to the icosahedral group, which has twofold (C_2), fivefold (C_5), and sixfold (C_6) rotation axes, horizontal reflection planes, inversion symmetry, and sixfold (S_6) and tenfold (S_{10}) improper rotations, for a total of 120 individual symmetry operations in all (Cotton, 1963).

XIII. CRYSTAL CHEMISTRY

In Chapter 3 we briefly described the structures of some classical superconductors, and in this chapter we provided a more detailed discussion of the structures of the cuprate superconductors. The question arises of how structure is related to the presence of metallic and superconducting properties.

Villars and Phillips (1988; Phillips, 1989a) proposed to explain the combinations of elements in compounds that are favorable for superconductivity at relatively high temperatures by assigning three metallic coordinates to each atom, namely an electron number N_e , a size r , and an electronegativity X . The electron numbers are given in Table 3.1 for most of the elements, with $N_e = 3$ for all of the rare earths and actinides; several correlations of N_e with T_c have already been given in Chapter 3. The sizes and electronegativities were determined empirically from a study of some 3,000 binary intermetallic compounds of types AB , AB_2 , AB_3 , and A_2B_5 . The resulting values for each atom are listed in Fig. 7.34 together with their electron numbers. These values, although arrived at empirically on the basis of the constraint of self-consistency, do have a spectroscopic basis, and thus are called, respectively, *spectroscopic radii* and *spectroscopic electronegativities*.

The metallic coordinates of the atoms can be employed to calculate the three Villars-Phillips (VP) coordinates for each compound, namely (a) average number of valence electrons $N_v = \langle N_e \rangle_{av}$, (b) spectroscopic electronegativity difference ΔX , and (c) spectroscopic radius difference ΔR , where we are using the VP notation. For example, for the compound NbN, with $T_c = 17.3$ K, we have, using the data from Fig. 7.34,

$$\begin{aligned} N_v &= \frac{1}{2}(4 + 5) = 4.5, \\ \Delta R &= 2.76 - 0.54 = 2.22, \\ \Delta X &= 2.03 - 2.85 = -0.82. \end{aligned} \quad (7.16)$$

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H 1 2.10* 1.25*																
Li 1 0.90 1.61	Be 2 1.45 1.08															
Na 1 0.89 2.65	Mg 2 1.31 2.03															
K 1 0.80 3.69	Ca 2 1.17 3.00	Sc 3 1.50 2.75	Ti 4 1.86 2.58	V 5 2.22 2.43	Cr 6 2.00 2.44	Mn 7 2.04 2.22	Fe 8 1.67 2.11	Co 9 1.72 2.02	Ni 10 1.76 2.18	Cu 11 1.08 2.04	Zn 12 1.44 1.88	Ga 3 1.70 1.695	Ge 4 1.99 1.56	As 5 2.27 1.415	Se 6 2.54 1.285	Br 7 2.83 1.20
Rb 1 0.80 4.10	Sr 2 1.13 3.21	Y 3 1.41 2.94	Zr 4 1.70 2.825	Nb 5 2.03 2.76	Mo 6 1.94 2.72	Tc 7 2.18 2.65	Ru 8 1.97 2.605	Rh 9 1.99 2.52	Pd 10 2.08 2.45	Ag 11 1.07 2.375	Cd 12 1.40 2.215	In 3 1.63 2.05	Sn 4 1.88 1.88	Sb 5 2.14 1.765	Te 6 2.38 1.67	I 7 2.76 1.585
Cs 1 0.77 4.31	Ba 2 1.08 3.402	La 3 1.35 3.08	Hf 4 1.73 2.91	Ta 5 1.94 2.79	W 6 1.79 2.735	Re 7 2.06 2.64	Os 8 1.85 2.65	Ir 9 1.87 2.624	Pt 10 1.91 2.70	Au 11 1.19 2.66	Hg 12 1.49 2.41	Tl 3 1.69 2.235	Pb 4 1.92 2.09	Bi 5 2.14 1.997	Po 6 2.40 1.90	At 7 2.64 1.83
Fr 1 0.70* 4.37*	Ra 2 0.90* 3.53*	Ac 3 1.10* 3.12*														
Ce 3 1.1* 4.50*	Pr 3 1.1* 4.48*	Nd 3 1.2* 3.99*	Pm 3 1.15* 3.99*	Sm 3 1.2* 4.14*	Eu 3 1.15* 3.94*	Gd 3 1.1* 3.91*	Tb 3 1.2* 3.89*	Dy 3 1.15* 3.67*	Ho 3 1.2* 3.65*	Er 3 1.2* 3.63*	Tm 3 1.1* 3.60*	Yb 3 1.1* 3.59*	Lu 3 1.2* 3.37*			
Th 3 1.3* 4.98*	Pa 3 1.5* 4.96*	U 3 1.7* 4.72*	Np 3 1.3* 4.93*	Pu 3 1.3* 4.91*	Am 3 1.3* 4.89*											

Figure 7.34 Periodic table listing metallic valences (upper right), sizes (center), and electronegativities (bottom) in the box of each element, according to the Villars-Phillips model (Phillips, 1989a, p. 321).

The VP coordinates for the A15 compound Ge_3Nb with $T_c = 23.2$ K are calculated as follows:

$$N_v = \frac{1}{4}(4 + 3 \times 5) = 4.75,$$

$$\Delta R = \frac{1}{2}(1.56 - 2.76) = -0.60, \quad (7.17)$$

$$\Delta X = \frac{1}{2}(1.99 - 2.03) = -0.02.$$

The text by Phillips (1989a) tabulates the VP coordinates for more than 60 superconductors with $T_c > 10$ K and for about 600 additional superconductors with transition temperatures in the range $1 < T_c < 10$ K.

When the points for the 600 compounds with lower transition temperatures are plotted on a three-dimensional coordinate system with axes N_v , ΔX , and ΔR , they scatter over a large range of values, but when the points for compounds with $T_c > 10$ K are plotted, they are found to cluster in three regions, called islands, as shown in Fig. 7.35. Island A contains the A15 compounds plus some complex intermetallics, island B consists mainly of the NbN family plus some borides and car-

bides, and island C has closely clustered Chevrel phases, with the high- T_c cuprates on the left. When ternary ferroelectric oxides with Curie temperatures that exceed 500°C are plotted in the same diagram as the superconductors they cluster between the Chevrel group and the cuprates. These ferroelectric oxides are not superconductors, though Phillips (1989a) suggested that doping them with Cu and alkaline earths could produce superconductors with high transition temperatures.

Thus we see that the high transition temperatures of classical superconductors are favored by particular structures and by particular combinations of metallic coordinates for each of these structures. The Villars-Phillips approach provides both structural and atomic criteria for the presence of high T_c .

We have discussed the Phillips approach to a crystal chemistry explanation of the superconductivity of the cuprates. Other researchers have offered alternate, in some cases somewhat related, approaches to understanding the commonali-

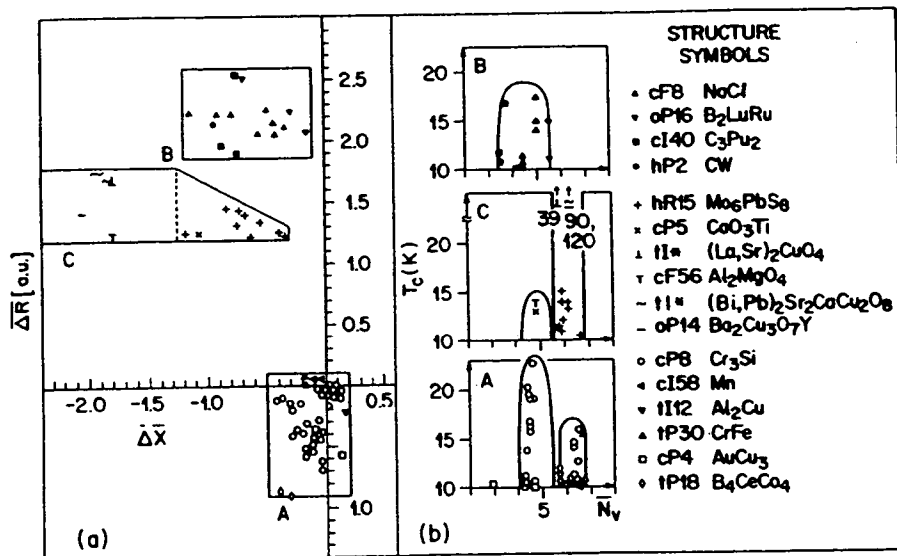


Figure 7.35 Regions in the Villars-Phillips configuration space where superconductivity occurs at relatively high temperatures (Phillips, 1989a, p. 324; Villars and Phillips, 1988).

ties of the various high-temperature and classical superconductors (Adrian, 1992; Schneider, 1992; Tajima and Kitazawa, 1990; Whangbo and Torardi, 1991; Torrace, 1992; Yakhmi and Iyer, 1992; Zhang and Sato, 1993).

XIV. COMPARISON WITH CLASSICAL SUPERCONDUCTOR STRUCTURES

Many elements such as copper and lead are face centered cubic, while many other elements, such as niobium, are body centered cubic, with $a = 3.30 \text{ \AA}$ for Nb. The A15 compounds, such as Nb_3Se , are (simple) cubic with lattice constant $a \approx 3.63\sqrt{2}$ and have parallel chains of Nb atoms 5.14 \AA apart. Other types of classical superconductors, such as the Laves and Chevrel phases, are cubic or close to cubic. The new oxide superconductors are tetragonal or orthorhombic close to tetragonal, and they all have $a \approx b \approx 3.85 \text{ \AA}$, which is somewhat greater than the value for the A15 compounds. The third lattice constant c varies with the compound, with the values 13.2 \AA for $LaSrCuO$, 11.7 \AA for $YBaCuO$, and ≈ 23 to 36 \AA for the

$BiSrCaCuO$ and $TlBaCaCuO$ compounds. These differences occur because the number of copper-oxygen and other planes per unit cell, as well as the spacings between them, vary from compound to compound due to the diverse arrangements of atoms between the layers. Thus relatively high-symmetry crystal structures are characteristic of many superconductors.

XV. CONCLUSIONS

Almost all the high-temperature oxide superconductors have point symmetry D_{4h} ($a = b$) or symmetry close to D_{4h} ($a \approx b$). These superconductors consist of horizontal layers, each of which contains one positive ion and either zero, one, or two oxygens. The copper ions may be coordinated square planar, pyramidal, or octahedral, with some additional distortion. Copper oxide layers are never adjacent to each other, and equivalent layers are never adjacent. The cations alternate sites vertically, as do the oxygens. The copper oxide layers are either flat or slightly puckered, in contrast to the other metal oxide layers, which are generally far from planar. The highest T_c compounds have metal layers

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FURTHER READING

The Wyckoff series, *Crystal Structures* (1963, Vol. 1; 1964, Vol. 2; 1965, Vol. 3; 1968, Vol. 4) provides a comprehensive tabulation of crystal structures, but many important classical superconductors such as the A15 compounds are not included. The *International Tables for X-Ray Crystallography* (Henry and Lonsdale, 1965, Vol. 1) provide the atom positions and symmetries for all of the crystallographic space groups. The Strukturbericht notation, e.g., A15 for Nb₃Ge, is explained in Pearson's compilation (1958).

Details of cuprate crystallographic structures are given by Beyers and Shaw (1989; YBa₂Cu₃O₇), Burns and Glazer (1990), Hazen (1990), Poole *et al.* (1988, Chapter 6), Santoro (1990), and Yvon and François (1989). Phillips (1989a) provides an extensive discussion of the crystal chemistry of the cuprates. Our earlier work (Poole *et al.*, 1988, p. 107) lists the site symmetries in perovskite and cuprate structures. Billinge *et al.* (1994) reviewed lattice effects in high temperature superconductors, and Zhu (1994) reviewed structural defects in YBa₂Cu₃O_{7-δ}.

The microstructure of high temperature superconductors studied by electron microscopy are reviewed by Chen (1990), Gai and Thomas (1992), Gross and Koelle (1994), and Shekhtman (1993). Oxygen stoichiometry in HTSC's is reviewed by Chandrasekhar *et al.*, (1994), Green and Bagley (1990) and by Routbert and Rothman (1995). Electron-doped superconductors are reviewed by Almasan and Maple (1991) and by Fontcuberta and Fàbrega (1995).

The March 1992 special issue of *Accounts of Chemical Research* (Vol. 25, No. 3) is devoted to reviews of buckminsterfullerenes. Two recent books are edited by Billups and Ciofolini (1993) and by Kroto and Walton (1993), and the review by Dresselhaus *et al.* (1994) are devoted to fullerenes. The thallium compounds were reviewed by Hermann and Yakhimi (1993) and the mercury superconductors by Chu (1995).

PROBLEMS

1. Show that the radius of the octahedral hole in an fcc close-packed lattice of atoms of radius r_0 is equal to $[\sqrt{2} - 1]r_0$. What is the radius of the hole if the lattice is formed from oxygen ions?
2. Show that the radius of the tetrahedral hole in an fcc close-packed lattice of atoms of radius r_0 is equal to $[(3/2)^{1/2} - 1]r_0$.

What is the radius of the hole if the lattice is formed from oxygen ions?

3. The "image perovskite" unit cell is generated from the unit cell of Fig. 7.1 by shifting the origin from the point (0,0,0) to the point $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Sketch this "image" cell. Show that the planes of atoms in this cell are the image planes related by the body centering operation to those of the original perovskite. This image cell is the one that usually appears to represent perovskite in solid-state physics texts.
4. Calculate the distance between the yttrium atom and its nearest-neighbor Ba, Cu, and O atoms in the superconductor YBa₂Cu₃O₇.
5. Write down the x, y, z coordinates for the five numbered atoms in the initial plane of Fig. 7.16. Give the explicit symmetry operations, with the proper choice of sign in Eq. (7.5) for each case, that transform these five atoms to their indicated new positions on the other three planes.
6. Explain how the international and Schönflies symbols, mmm and D_{2h} respectively, are appropriate for designating the point group for the orthorhombic superconductors.
7. What are the symmetry operations of the A15 unit cell of Fig. 3.19?
8. The D_{2h} point group consists of eight symmetry operations that leave an orthorhombic cell unchanged, namely an identity operation E that produces no change, three twofold rotations C_2^i along $i = x, y, z$, three mirror reflection planes σ_{ij} , and an inversion i . Examples of these symmetry operations are

E	$x \rightarrow x$	$y \rightarrow y$	$z \rightarrow z$
C_2^x	$x \rightarrow x$	$y \rightarrow -y$	$z \rightarrow -z$
σ_{xy}	$x \rightarrow x$	$y \rightarrow y$	$z \rightarrow -z$
i	$x \rightarrow -x$	$y \rightarrow -y$	$z \rightarrow -z$

A group has the property that successive application of two symmetry oper-

ations produces a third. Thus, we have, for example,

$$C_2^x \sigma_{xy} = \sigma_{zx}$$

$$C_2^y C_2^x = C_2^z$$

$$i C_2^y = \sigma_{zx}$$

$$\sigma_{zx} \sigma_{yz} = C_2^z.$$

These results have been entered into the following multiplication table for the D_{2h} group. Fill in the remainder of the table. Hint: each element of a group appears in each row and each column of the multiplication table once and only once.

	E	C_2^x	C_2^y	C_2^z	i	σ_{xy}	σ_{yz}	σ_{zx}
E								
C_2^x								
C_2^y								
C_2^z								
i								
σ_{xy}								
σ_{yz}								
σ_{zx}								

- Construct the multiplication table for the D_{4h} point group which contains the 16 symmetry elements that leave a tetragonal unit cell unchanged. Which pairs of symmetry elements A and B do not commute, i.e., such that $AB \neq BA$? Hint: follow the procedures used in Problem 8.
- Draw diagrams analogous to those in Fig. 7.25 for the first two members of the aligned series $\text{TiBa}_2\text{Ca}_n\text{Cu}_{n+1}\text{O}_{5+2n}$, where $n = 0, 1$.
- Draw the analogue of Fig. 7.19 for the Nd_2CuO_4 compound, showing the location of all of the Cu and O atoms. How do Figs. 7.21 and 7.22 differ for Nd_2CuO_4 ?
- Calculate the Villars–Phillips coordinates for the three superconductors MoP_3 , V_3Sn , and NbTi .
- Select one of the compounds ($\text{Ti}_2\text{Ba}_2\text{CuO}_6$, $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, $\text{Ti}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_6$) and construct a table for it patterned after Tables 7.5 or 7.6.
- Locate a twofold (C_2), fivefold (C_5), and sixfold (C_6) rotation axis, and also a reflection plane σ_h in the buckyball sketch of Fig. 3.35. How many of each type of operation are there?
- We can see by examining Fig. 3.35 that a buckyball has inversion symmetry. Identify a sixfold (S_6) and tenfold (S_{10}) improper rotation axis, where an improper rotation is understood to involve a sequential inversion and a proper rotation. How many S_6 and how many S_{10} axes are there?
- Show that the total number of edges E in a fullerene is given by

$$E = \frac{1}{2} \sum_s s F_s,$$
 and the number of vortices is

$$V = \frac{1}{3} \sum_s s F_s,$$
 where F_s is the number of faces with s sides.
- Show that the cubic fullerene compound C_8 has nine resonant structures.

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